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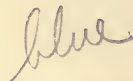|	
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HIGHER MATHEMATICS
FOR
CHEMICAL STUDENTS

BY

blue

J. RIDDICK PARTINGTON, B.Sc.
FELLOW OF MANCHESTER UNIVERSITY

WITH FORTY-FOUR DIAGRAMS

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CONTENTS

APPENDICES

"Man kann nicht mathematisch beweisen, dass die Natur so sein müsse, wie sie ist."—(E. MACH)

HIGHER MATHEMATICS FOR CHEMICAL STUDENTS

INTRODUCTION

NATURAL Science is that branch of knowledge which is concerned with the complete investigation of what we may call the "outer world," as distinguished from consciousness. The constant succession of our experiences we attribute to concomitant change in the objects of experience; we recognize the existence of phenomena. The succession of phenomena, on careful investigation, is found to have one predominating peculiarity; phenomena are related in experience. They do not pass unconnected, or in random fashion, as though due to a "fortuitous concourse of atoms"; they are, on the contrary, distinctly connected. It is this relation of phenomena which gives a definite meaning to science. By reason of past experiences, either individual or those preserved in the progress of the race, we are able more or less to foretell the future course of phenomena; we form "an expectation of a connexion between possible experiences," which Ostwald identifies with a so-called law of nature. We have no guarantee that the expectation will be fulfilled; all we can say is that in every case observed up to the present it has been fulfilled, and the probability is very great that the connexion will also appear in the next case which comes under our observation.

The statement of a law of nature involves the formation of a concept, or general idea, in which the likenesses of phenomena are collected, and the differences, in so far

1

as they are not intimately involved in the nature of the case, are eliminated. The formation of such a concept involves three stages, in which we successively *compare* the various experiences, or percepts ; *abstract* those qualities which seem to have a likeness ; and *generalize* by arranging our experiences under names, a name being a symbol for a general idea. According to the degree of our success, the name will be so exact as to be capable of *definition*, whereby the parts involved in the concept are set in relation to the parts of other concepts. In this way an emergence into clearness and distinctness is evident, and the degree of clearness and distinctness of the final product of a mental operation is an indication of the extent to which that process has been successful.

Every person, even the savage, has formed a definite number of concepts ; but the concept formed will obviously depend for its completeness and accuracy upon the number and nature of the experiences which go to form the raw material of the concept. The names "sulphur," "force," "circle" will recall very different ideas in different persons. In the former example, most persons will recall the properties of yellow colour, brittleness, combustibility, etc., and the group of these essentials, abstracted from such non-essential properties as size, shape, temperature, etc., will form the concept to which they attribute the name "sulphur". To a person whose experience has never been brought into relation with the object sulphur, the name signifies nothing ; to the scientist it signifies much more than to the ordinary person, his concept involves the ideas of specific gravity, crystalline form, element, atom, and the like, derived from past experiences. His concept is distinguished from the other by involving the concept of *number* or *quantity.*

"I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it ; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of

a meagre and unsatisfactory kind; it may be the beginning
of knowledge, but you have scarcely in your thoughts ad-
vanced to the stage of science" (Lord Kelvin, 1883).

The earliest chemical theory was qualitative in the
strictest sense; the so-called Aristotelean doctrine of the
four elements assumed that air, water, earth, and fire, were
qualities impressed on a primal matter; and the changes
of material bodies were explained by the assumption that
properties could be taken up by, and impressed upon, or
removed from, the base-stuff. Transmutation as a possi-
bility followed at once, and centuries of vain endeavour
were required to impress the fact of its impossibility, lead-
ing to the true concept of *element* (Robert Boyle, "The
Sceptical Chymist," London, 1661). "And therefore I
think you have done very wisely to make it your business
to consider the *Phænomena* relating to the present
question, which have been afforded by experiments, especi-
ally since it might seem injurious to our senses, by whose
mediation we acquire so much of the knowledge we have
of things corporal, to have recourse to far-fetched and ab-
stracted Ratiocination, to know what are the sensible in-
gredients of those sensible things that we daily see and
handle, and are supposed to have the liberty to untwist (if
I may so speak) into the primitive bodies they consist of"
. . . "being Gentlemen and very far from the litigious
humour of loving to wrangle about words or terms or
notions as empty; they had before his coming in, readily
agreed promiscuously to use when they pleased Elements
and Principles as terms equivalent: and to understand
both by the one and the other, those primitive and simple
bodies of which the mixt ones are said to be composed,
and into which they are ultimately resolved" (Boyle, loc.
cit. pp. 15, 16).

The quantitative investigations of Black on the burn-
ing of lime and magnesia alba, in which the balance (pre-
viously characterized by the French chemist Jean Rey as
"an instrument for clowns") was applied at every turn,

led to the rejection of a hypothetical "principle of causticity," and replaced it by a "sensible ingredient of a sensible body," fixed air. The extension of Black's method by the physicist Lavoisier led to the downfall of the purely qualitative theory of phlogiston, and gave to chemistry the true methods of investigation, and its first great quantitative law—the law of conservation of matter. Wenzel and Richter, the latter, as we shall see later, of most pronounced mathematical temperament, laid the foundations of stoichiometry, or "the art of measuring the chemical elements"; and Dalton, the mathematical tutor, following up the lead of Newton, combined the whole of the results of quantitative measurement which had accumulated up to his time, in a comprehensive theory, based on the concept of the chemical atom.

The results of a scrutiny of the materials of chemical science from a mathematical standpoint are pronounced in two directions. In the first we observe crude qualitative notions, such as fire-stuff, or phlogiston, destroyed ; and at the same time we perceive definite measurable quantities such as fixed air, or oxygen, taking their place. In the second direction we notice the establishment of generalizations, laws, or theories, in which a mass of quantitative data is reduced to order and made intelligible. Such are the law of conservation of matter, the laws of chemical combination, and the atomic theory.

As an instance of the remarkably far-reaching effect which a single mathematico-physical concept has had upon the development of chemical theory, one has but to recall the state of chemistry just before the revival of Avogadro's law by Cannizzaro, to be impressed by its confusion. Relying solely upon their "chemical instinct," the leaders of the various schools of chemical thought had developed each his own theoretical system. Types, radicals, copulæ, atoms, equivalents, mixing-weights, and a host of other conceptions strove for supremacy. The strife was stilled, order and unity were restored, as soon as Avogadro's great

idea was seen in its true light, and the concept of the molecule was introduced into chemistry. A formula which had required pages of reasoning from a purely chemical standpoint to establish, and that insecurely, was fixed by a single numerical result. There are not wanting, even to-day, chemists who advocate " purely chemical " methods in chemistry, and cannot appreciate the value of physical evidence in conjunction with mathematical calculations. We can only hope that their number is decreasing exponentially with time.

From the time when Guldberg and Waage gave quantitative form to the speculations of the physicist Berthollet, a clear conception of chemical equilibrium, in sharp contrast to an anthropomorphic theory of affinity dating back to Hippocrates and Barchausen, has yielded rich and abundant fruit.

The philosopher Comte has made the statement that chemistry is a non-mathematical science. He also told us that astronomy had reached a stage when further progress was impossible. These remarks, coming after Dalton's atomic theory, and just before Guldberg and Waage were to lay the foundations of chemical dynamics, Kirchhoff to discover the reversal of lines in the solar spectrum, serve but to emphasize the folly of having " recourse to far-fetched and abstracted Ratiocination," and should teach us to be " very far from the litigious humour of loving to wrangle about words or terms or notions as empty ".

Jeremias Benjamin Richter in his " Anfangsgründe der Stöchyometrie, oder Messkunst chemischer Elemente," published by J. F. Korn of Breslau, in two volumes (1792), strikes a very decided note when he repeats a statement from his Inaugural Dissertation (" de Usu Matheseos in Chymia," Königsberg, 1789) which must have puzzled his contemporaries : " chemistry belongs, in its greatest part, to applied mathematics ". The reason why so little progress is made on the mathematical side of chemistry is, says Richter, that " the most prominent chemists occupy

themselves little with mathematics, and the mathematicians feel that they have little business in the province of chemistry ". The mathematical equipment of chemists must certainly have been somewhat restricted, for Richter begins his book by about thirty pages of mathematical introduction, in which he explains the arithmetical operations, and the rudiments of algebra, concluding with an account of arithmetical and geometrical progressions ; this being doubtless as much as the chemist could then be expected to assimilate.

" The ultimate aim of pure science is to be able to explain the most complicated phenomena of nature as flowing by the fewest possible laws from the simplest possible data. A statement of a law is either a confession of ignorance, or a mnemonic convenience. It is the latter if it is deducible by logical reasoning from other laws. It is the former when it is only discovered as a fact to be a law. While on the one hand, the end of scientific investigation is the discovery of laws, on the other, science will have reached its highest goal when it shall have reduced ultimate laws to one or two, the necessity of which lies outside the sphere of our cognition. These ultimate laws—in the domain of physical science at least—will be the dynamical laws of the relation of matter to number, space, and time, themselves. When these relations shall be known, all physical phenomena will be a branch of pure mathematics " (Prof. Hicks, B. A. Address, Section A, 1895).

An explanation of a phenomenon is regarded, apparently instinctively, as the most general possible when it is a *mechanical* explanation. The " mechanism " of the process is the ultimate goal of experiment. Now this mechanism in general lies beyond the range of the senses ; either by reason of their limitations, as in the case of the atomic structure of matter, or by the very nature of the supposed mechanism, as in the theory of the ether. The only way to bridge the gap between the machinery of the physical process and the world of sense-impressions is to

think out some consequence of that mechanism. This we will call the *hypothesis*. The hypothesis, resting still on the mechanical basis, is yet beyond the range of direct experimental investigation ; but if, by mathematical reasoning, a consequence of the hypothesis can be deduced, this will often lie within the range of experimental inquiry, and thus a test of the soundness of the original mechanical conception may be instituted. Briefly, therefore, we may represent the intervention of mathematics in the study of physical science by the sequence :—

(Mechanism) ←→ Hypothesis ←→ Consequence ←→
(Range of the Senses)

The intermediate steps involve the mathematical operations.

As an illustration, consider that conception of the structure of matter which regards it as composed of discrete particles. If we make the hypothesis that a gas consists of such particles in motion, and obeying the laws of dynamics, we come to the Kinetic Theory of Gases. The hypothesis is still expressed in terms of the supposed mechanism, and its verification is yet out of reach. But if we develop mathematically this simple idea, we are led to a great number of relations between the sensible and measurable physical properties of gases ; and the good accord between these results and the results of experimental inquiry serves to strengthen our belief in the validity of the original hypothesis, and thence in the primary conception of the discrete partition of matter in space.

If the results of experimental inquiry, which we have reason to believe is technically accurate, are in discord with mathematical deductions from a hypothesis, two courses are open. Either the theory may be abandoned, at least for a time, or else it may be modified. Disagreement between theory and experiment has proved a most potent agent in broadening theoretical views, and in making clear the necessity for new concepts or hypotheses

Van der Waals' extension of the gas laws, which had been deduced from a kinetic hypothesis assuming a simpler mechanism for the structure of gaseous matter than is really involved, is a case in point. It is necessary to guard against a possible danger in this connexion, namely that of submitting too readily to the result of a so-called "crucial experiment". Very few experiments can, in the nature of things, be really crucial. One so-called "crucial experiment" which decided between Newton's corpuscular theory of light and Huyghens' wave-theory, viz. the relation between the law of refraction and the velocity of light, was not at all decisive. As Preston says ("Theory of Light," second edition, p. 19): "We believe an ingenious exponent of the emission theory, by suitably framing his fundamental postulates, might fairly meet all the objections that have been raised against it". In fact, we perceive clearly that theories and hypotheses are not accepted or rejected outright; they have their periods of activity, and then lie dormant for a time, only to be revived in a new form later on. The fundamental materials from which we construct our picture of the universe may appear in different shapes, but there is really very little discontinuity between what seem at first sight very different views.

All measurements are made through the medium of the senses, and theories result from operating on such measurements with the instruments of mathematics. It is clear, however, that the distinguishing mark of the whole development of theoretical chemistry and physics is the elimination of the anthropomorphic elements, especially specific sense-impressions, from the concepts. This process is called by Prof. M. Planck ("Acht Vorlesungen über theoretische Physik"; Hirzel, Leipzig, 1910) the *objectification* of the physical system. Thus, in early physical systems we have optics dealing with phenomena perceived by the eye; acoustics treating of auditory percepts, and so on. The subjective concepts of "tone" and

" colour" have now been replaced by the objectified concepts of frequency of vibration ; and wave-length. The object of this process of elimination is, according to Planck, the striving towards a unification of the whole theoretical system, so that it shall be equally significant for all intelligent beings. " Jeder grosse physikalische Gedanke bedeutet einen weiteren Schritt in der Emanzipation vom Anthropomorphismus."

Whether this will be fully realized or not we cannot say ; in any case the method of attack on the unknown still remains the same : " In comparing the science of the past, the present, and the future, in placing the particulars of its restricted experiments side by side with its aspirations after unbounded and infinite truth, and in restraining myself from yielding to a bias towards the most attractive path, I have endeavoured to incite in the reader a spirit of inquiry which, dissatisfied with speculative reasonings alone, should subject every idea to experiment, to encourage the habit of stubborn work, and excite a search for fresh chains of evidence to complete the bridge over the bottomless unknown " (D. Mendeléeff, " Principles of Chemistry," English translation, 1905, p. viii, Vol. I).

Chapter I

FUNCTIONS AND LIMITS

1. FUNCTIONS

IT has been shown that the business of scientific investigation is the tracing out and classifying of the relations existing between phenomena. The first duty of mathematics in the service of physical science is to provide a method of expressing this relationship between phenomena, without, for the present, attempting to specify more definitely the quantitative aspect of the problem. The study of the mathematical representation of the connexion between phenomena will occupy us at the very outset.

Let us suppose that we have a flask containing water and its vapour, and connected with a manometer for measuring the pressure exerted by the vapour. If the water is heated at a definite temperature, and the readings of the manometer recorded for different temperatures, one obtains a table of vapour-pressures :—

Temperature ° C.	Pressure cm.	Temperature ° C.	Pressure cm.
– 10	0·2151	60	14·89
0	0·4569	70	23·33
+ 10	0·9140	80	35·49
20	1·7363	90	52·55
30	3·151	100	76·00
40	5·49	110	107·5
50	9·20		

A consideration of this table will illustrate the meaning of several forms of expression constantly used in mathematics. We observe that:—

(1) The pressure depends on the temperature in such a way that if any particular temperature is chosen arbitrarily there is one, and only one, definite pressure which corresponds with the definite chosen temperature. Both the temperature and pressure are capable of assuming different values; they are called *Variables*. If we agree to alter the temperature in 10° steps, and measure the pressure corresponding to each temperature, we may call the temperature, the values of which are determined by arbitrary choice, the *independent variable* ; the pressure, which must take up a particular value corresponding to each arbitrarily chosen temperature, and is therefore completely determined by the temperature, is called the *dependent variable*. If the pressures had been arbitrarily chosen, and the temperatures corresponding to each pressure determined, then the pressure would be the independent, the temperature the dependent, variable.

(2) When one variable magnitude depends upon another (or several others) in such a way that, if the value of the latter be fixed, the former must assume one or more definite values, then the first magnitude is said to be a *Function* of the other, or others. The first magnitude is the dependent, the second the independent, variable. By way of notation we say that if the pressure p is the dependent variable, and t, the temperature, is the independent variable, then

$$p \text{ is a function of } t, \text{ or}$$
$$p = f(t) \quad . \quad . \quad . \quad . \quad (1)$$

The symbol "f" means "a function of" the magnitude enclosed in the brackets.

This equation states that the value of p is determined by that of t, in the case of the vapour-pressure of a liquid p is a function of t alone. If we had considered a *gas*, then p would have depended on the volume v as well as on

the temperature t; for if only t had been fixed by arbitrary choice, p would still be undetermined, and could take up a range of values depending on the value of v. If t and v are fixed, then p takes up a definite value. In this case

$$p = f(t, v) \qquad . \qquad . \qquad . \qquad (2)$$

If x is the independent variable, y the dependent variable, the functional relation between x and y is expressed by the equation

$$y = f(x) \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

Instead of "f," other symbols are often used; thus $F(x)$, $\phi(x)$, $\psi(x)$.

If y is a function of several variables $x_1, x_2, x_3, \ldots$ then

$$y = f(x_1, x_2, x_3, \ldots) \qquad . \qquad . \qquad (4)$$

The vapour-pressure of a solution depends on the composition as well as on the temperature. If the composition is expressed in terms of the concentration c as one independent variable

$$p = f(t, c).$$

These equations are perfectly general; they express the fact that one magnitude is related to others in a fixed and definite way. Whether this relationship can be represented by a mathematical expression is another matter. "All that is necessary to establish a functional relation between two variables is that, when other things are unaltered, the value of one shall determine that of the other" (Lamb). In the case of gas-pressure, the expression is known to be

$$p = \text{constant} \times (t + 273) \times c.$$

The corresponding expression for the vapour-pressure of a liquid is not yet known.

According to Ostwald ("Principles of Inorganic Chemistry," trans. Findlay, p. 73), the content of a quantitative law of nature can be expressed by saying that it represents two (or several) measurable properties of a system as functions of one another.

If the same symbol is used in any investigation for two

functions, these have been formed in the same manner. Thus

$$\text{if } f(x) = x^2,$$
$$\text{then } f(y) = y^2;$$
$$\text{and if } \phi(x) = 1/x,$$
$$\text{then } \phi(y) = 1/y.$$

(3) If, corresponding with a fixed set of values of the independent variables, there is only one definite value of the dependent variable, the latter is called a *single-valued function* of the former. But if more than one value of the dependent variable can correspond with a fixed set of
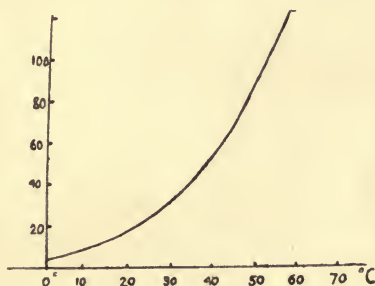

Fig. 1.

values of the independent variables, the function is called a *multi-valued function*.

The relations are rendered very evident by using the *graphical method*, invented by the great French mathematician René Descartes (*b.* 1596, *d.* 1650). By a series of measurements, or by calculation, we find pairs of corresponding values of the variables, say (x_1, y_1), (x_2, y_2), (x_3, y_3), ... Taking a horizontal straight line $x'x$, we measure off to the right distances proportional to the magnitudes x_1, x_2, x_3, ..., starting from an arbitrarily chosen zero point 0. From the points x_1, x_2, ... are erected perpendiculars proportional to the magnitudes y_1, y_2, ... The points (x_1, y_1), (x_2, y_2), ... are then joined by an unbroken

line, which indicates in a striking manner the way in which y changes with x. If two or more points lie on the same perpendicular the function is multi-valued. The curve of the vapour-pressures of water is given in fig. 1.

(4) If the temperature is altered, the vapour-pressure changes. Suppose that successive temperature changes are made smaller and smaller, say $1°$, $0.1°$, $0.01°$, ..., then the change of vapour-pressure consequent on a change of temperature becomes smaller as the temperature interval decreases. This holds down to a point where the changes are too small to measure ; we can, however, continue the process mentally, and imagine that an infinitely small change in the value of the independent variable will produce an infinitely small change in the value of the function. A function possessing this property is called a continuous function.

2. CONTINUITY

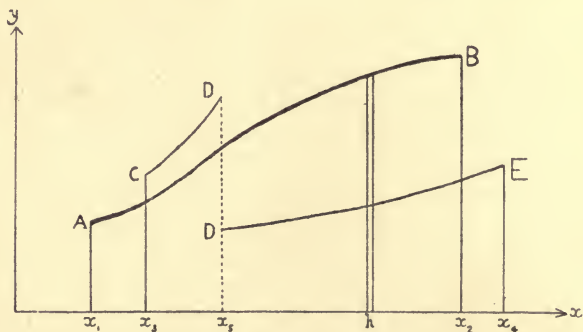A glance at the two curves AB, CDD¹E, of fig. 2 will reveal a marked difference between them. Whereas the

FIG. 2.

curve AB runs from start to finish without break, the curve CD¹DE breaks suddenly at the point D¹, recommencing at D. The curve AB is *continuous*, whilst

CD¹DE is *discontinuous*. If we regard each curve as the graph of a given function, it is evident that we must distinguish between two kinds of functions; continuous functions, and discontinuous functions. We now proceed to give the condition which the function must satisfy in order that it shall be a continuous function, and to show that if the function does not satisfy this condition its graph will be of the form CD¹DE (or other forms which will be described).

Let $f(x)$ be a given function of x.

This function will be continuous, for all values of x lying between the limits x_1 and x_2, if, for all these values of x the numerical value of the difference

$$f(x + h) - f(x)$$

diminishes indefinitely with h, or is infinitesimally small at the same time as h. In other words, we can choose a value of h which will make the value of $f(x + h) - f(x)$ less than any magnitude we choose to name, however small.

We can show that $f(x) = x^2$ satisfies this condition. Suppose that the continuity of this function had been challenged by an opponent. We should then ask him to name a very small magnitude such that $f(x + h) - f(x)$ would be greater in numerical value than the chosen magnitude. Suppose that one millionth $= 10^{-6}$ had been chosen. It would be sufficient to show that a value of h could be chosen so that, for a fixed value of x, $f(x + h) - f(x)$ would be less than 10^{-6}. Now

$$f(x + h) - f(x) = (x + h)^2 - x^2 = 2xh + h^2.$$

If x is fixed, it is always possible to find a value of h such that

$$2xh + h^2 = 10^{-6},$$

because this value is simply the positive root of the quadratic equation. If h is now chosen less than this value, the difference will be less than 10^{-6}, and the opponent's objection is refuted. He might now choose 10^{-10} as the value; but we could proceed in exactly the same way and

find a value of h such that for all values of h less than the value so found, the numerical value of the difference $f(x + h) - f(x) = (x + h)^2 - x^2$ would be less than 10^{-10} for a fixed value of x. The same process would apply to any magnitude, however small, and the continuity of $f(x) = x^2$ would therefore be established in accordance with the definition. In a similar way we could proceed to test any other function, such as $f(x) = x^3$, which might come under consideration.

It is now easy to see that the curve AB is the graph of a continuous function. Let h be a small increment of x,
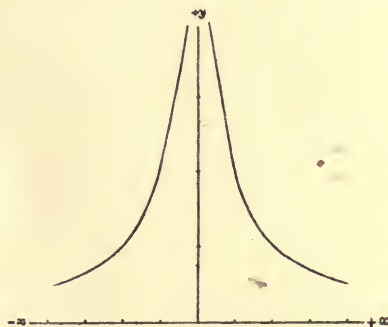

FIG. 3.

from any value lying to the right of x_1 and to the left of x_2, to a value lying in the same range. If perpendiculars are erected from the extremities of this small length on the x-axis so as to meet the curve, then

$$f(x + h) - f(x)$$

will be the difference between the lengths of these perpendiculars. Now it is at once obvious, from the form of the curve, that this distance diminishes as h diminishes, and that it can be made as small as we please by taking h small enough. But this is the condition for the continuity of $f(x)$.

We can now show that the curve CD^{1}DC does not

satisfy such a condition. For let a small distance h be taken so that its extremities lie on opposite sides of x_5. If ordinates are erected to meet the curve, one will meet the portion CD^1, the other the portion DE; and if h is made smaller and smaller so that its extremities always lie on opposite sides of x_5, the difference between the lengths of the ordinates can never be made less than DD^1, however small h may be. The curve is therefore *discontinuous* at the value $x = x_5$.

Another type of discontinuity is shown by functions which become infinite for particular values of the variable.

$$\text{Thus } f(x) = \frac{1}{x}$$

becomes infinite for $x = 0$. The curve consists of two branches, each branch running up to infinity at $x = 0$.

If h is a small positive or negative value of x, then *when* $x = 0$, the numerical value of $f(x + h) - f(x)$ is always infinity no matter how small h may be. The function therefore fails to satisfy the condition for continuity at the point $x = 0$, although it does so at all other points.

3. ALGEBRAIC FUNCTIONS

These are obtained by performing with the variable and known constants any finite number of operations of addition, subtraction, multiplication, division, and extraction of integral roots.

$$\text{e.g. } 2x, \ x^2, \ \sqrt{x}.$$

If the operations include addition, subtraction, multiplication, and division only, the function is a *rational* function; and all such functions can be reduced to the form

$$F(x)/f(x),$$

where $F(x)$ and $f(x)$ are *rational integral functions*, i.e. each is made up of a finite number of terms of the form

$$Ax^m,$$

where m is a whole number, and A a constant.

2

The rational integral function

$$y = f(x) = a + bx,$$

where a and b are constants, is represented graphically by a straight line, and is called a *linear function*. The expansion of a gas with rise of temperature at constant pressure was found by Gay Lussac to be represented by the equation

$$v = v_0(1 + at),$$

where v, v_0 are the volumes at $t°$ C. and $0°$ C. respectively, and a is the coefficient of expansion. Obviously v is a linear function of t, the constants being

$$a = v_0,$$
$$b = v_0a.$$

Linear functions occur frequently in physical chemistry, especially in the study of dilute solutions.

A rational integral function of the form

$$y = f(x) = a + bx + cx^2,$$

where a, b, c are constants, is called a *parabolic function*. Callendar has found that the electrical resistance of a platinum wire is a parabolic function of the temperature at all temperatures from that of boiling liquid air ($-190°$ C.) to that of melting platinum ($1500°$ C.). That is

$$R = R_0(1 + at + bt^2),$$

where $R_0 = $ resistance at $0°$ C., and a, b are constants.

The statement that one quantity "is a function" of another, or of others, occurs frequently in treatises on physical chemistry, especially those dealing with the subject in its thermodynamic aspect. Students are often puzzled by the apparently abstract nature of the term "function"; the following example may make the matter a little clearer.

Consider a quantity of a gas, say air, enclosed in a vessel, so that its mass remains constant. There are three possible ways in which the state of the gas may be altered, viz. by change of volume, of pressure, and of temperature. If two of these variables have been fixed by arbitrary choice, the third then takes up a perfectly definite value,

over which we have no control. As Gibbs proposed, we say that a gas has two degrees of *independent variability*, or two *degrees of freedom*. The same is true of any homogeneous body; solid, liquid, or gas.

Now suppose we keep the temperature constant, and alter the volume. The pressure alters at the same time, it therefore depends on the volume, and alters when the volume alters. By definition, we therefore say that "the pressure is a function of the volume," or

$$p = f(v) \text{ when } t \text{ is constant.}$$

Experiments with a Boyle's law tube show what the "form" of this function is; in other words, they enable us to pass from this very general equation (which is in fact true for liquids and solids as well as gases) to a special equation which shows exactly what the relation is which exists between p and v. This is of course

$$p = \frac{h}{v} \text{ when } t \text{ is constant,}$$

or the pressure is inversely proportional to the volume. This statement is Boyle's law.

Now let the volume be kept constant, and the temperature be changed. The pressure is again altered, therefore

$$p = \phi(\theta) \text{ when } v \text{ is constant,}$$

where θ is the absolute temperature.

Experiment shows that in this case

$$p = h'\theta, \text{ when } v \text{ is constant,}$$

or the pressure is proportional to the absolute temperature when the volume is constant.

Now suppose that both volume and temperature are allowed to change simultaneously. The pressure is then a function of both, or

$$p = F(v, \theta).$$

Let p_1, v_1, θ_1 be the initial; p_2, v_2, θ_2, the final values of the variables. Let the change be imagined as brought about in two steps:—

(i) Change v_1 to v_2, keeping θ_1 constant. Let the

pressure then become p (not p_2, because the temperature is still θ). By Boyle's law

$$p_1 v_1 = p v_2 = k, \text{ when } \theta_1 \text{ is constant.}$$

$$\text{Thence } p = \frac{p_1 v_1}{v_2}.$$

(ii) Keeping the volume constant at v_2, let the temperature be changed to θ_2. The pressure must now become p_2, because v_2, θ_2 are the two independent variables characterizing the first state.

$$\text{But } p = h'\theta_1,$$
$$p_2 = h'\theta_2,$$
$$\therefore \frac{p}{\theta_1} = \frac{p_2}{\theta_2},$$
$$\therefore p\theta_2 = p_2\theta_1.$$
$$\text{But } p = \frac{p_1 v_1}{v_2},$$
$$\therefore \frac{p_1 v_1}{\theta_1} = \frac{p_2 v_2}{\theta_2} = r \text{ say.}$$
$$\text{Thus } p_1 v_1 = r\theta_1,$$
$$p_2 v_2 = r\theta_2,$$

and generally, for a constant mass of gas,

$$pv = r\theta.$$

Another way of stating this relation is often met with. We see that

$$p = \frac{r\theta}{v},$$

or p is proportional to $\dfrac{\theta}{v}$, which is written

$$p \propto \frac{\theta}{v},$$

i.e. "p varies as θ/v".

But $p \propto 1/v$ when θ is constant,

and $p \propto \theta$ when v is constant,

and the above shows that

$$p \propto \frac{1}{v} \times \theta \text{ when both } v \text{ and } \theta \text{ vary.}$$

This relation between variables which are proportional is quite general.

> If A *varies as* B *when* C *is constant*,
> and A *varies as* C *when* B *is constant*,
> then A *varies as* BC *when both* B *and* C *vary*.
> That is, if $A \propto B$ when C is constant,
> and $A \propto C$ when B is constant,
> then $A \propto BC$ when both B and C vary.

Notice the distinction between the two statements :

> (i) " y varies *with* x " :
> $$y = f(x).$$
> (ii) " y varies *as* x " :
> $$y = kx,$$

where k is a constant.

4. LIMITING VALUES

If a variable, changing in accordance with some assigned law, can be made to *approach* a fixed constant value as nearly as we please, without actually ever becoming equal to it, the constant is called the *limiting value*, or the *limit*, of the variable under these circumstances.

$$\text{Let } y = f(x).$$

If, when x is made to approach nearer and nearer to a fixed value, say a, y, as defined by the equation, tends more and more to another fixed value, say β, then β is called the limiting value of $y = f(x)$ for the value $x = a$. This is written

$$\text{Lim } f(x) = \beta,$$
$$x \to a$$

the symbol $\to$ meaning " approaches ".

Consider the fraction

$$y = \frac{2x + 3}{x + 1}.$$

This can be written in the form

$$\frac{2 + \dfrac{3}{x}}{1 + \dfrac{1}{x}}$$

If x is made larger and larger, the fractions $3/x$ and $1/x$ become smaller and smaller; and if we imagine x to be increased until it is greater than any assignable magnitude, however great, then $3/x$ and $1/x$ become smaller than any assignable magnitude, however small. We say shortly that

when x is *infinite*,
$3/x$ and $1/x$ are *zero*;

meaning that as x approaches the value infinity (∞), $1/x$ and $3/x$ approach the limiting value zero (0). This is written

$$\operatorname{Lim}_{x \to \infty} \frac{3}{x} = 0,$$

$x \to \infty$ meaning "x tends to infinity," and

$$\operatorname{Lim}_{x \to \infty} \frac{1}{x} = 0.$$

Hence
$$\operatorname{Lim}_{x \to \infty} y = \frac{2}{1} = 2.$$

Another example is the Infinite Series

$$1 + \tfrac{1}{2} + \tfrac{1}{4} + \tfrac{1}{8} + \ldots \qquad \text{ad inf.}$$

If we add the $\tfrac{1}{2}$ to the 1, the $\tfrac{1}{4}$ to the $1 + \tfrac{1}{2}$, the $\tfrac{1}{8}$ to the $1 + \tfrac{1}{2} + \tfrac{1}{4}$, and so on, we increase the sum at each step. But after twelve steps the term added is 0·0002, and successive terms continually decrease as we pass along the series. The sum tends to a limiting value, y, the greater the number of added terms; and it is easily proved that this limiting value, when the number of terms tends to infinity, is 2. Thus the "sum" of an infinite series may be finite.

Examples on Limits :—

(1) Find the limiting value of $\dfrac{x^2 + 3x - 4}{x(x - 1)}$ when $x \to 1$.

[5.]

(2) Show that the value of $1/(x - a)$ must instantane-

ously change from $-\infty$ to $+\infty$ as x passes through the value a.

(3) Find the limit of $\dfrac{x^2 + 2x - 8}{x^2 + 7x - 18}$ when $x \to 2$. $\left[\dfrac{6}{11}.\right]$

(4) Find the limit of $\dfrac{x + x^2}{x^2}$ when $x \to \infty$. [1.]

(5) Find the limit of $\dfrac{\sqrt{(x - 1)}}{\sqrt{x} - 1}$ when $x \to 1$.

Put $\sqrt{x} = 1 + h$, so that h vanishes for $x = 1$.

$$\text{Let } \frac{\sqrt{(x - 1)}}{\sqrt{x} - 1} = y$$

$$\therefore y^2 = \frac{2}{h} + 1.$$

When $h \to 0$ (i.e. $x \to 1$), $2/h \to \infty$

$$\therefore \text{Lim} \frac{\sqrt{x - 1}}{\sqrt{x} - 1} \to \infty$$

$$x \to 1$$

5. GEOMETRICAL ILLUSTRATIONS OF LIMITS

The conception of a limiting value, or limit, has played a very important part in the development of geometry as well as in the analytical branches of mathematics. The properties, and mensuration, of plane and solid figures bounded by straight lines can be treated in a fairly easy manner. But when the figures are bounded by curves, it is necessary to resort to the method of limits. A figure bounded by straight lines is constructed so that it lies outside or inside the given curved figure. If the volume (or area) of this figure is found, and if this figure approaches the curved figure in volume or area as the number of its sides is continually increased, then the volume or area of the curved figure is the limit of that of the rectilinear figure.

The circumference of a circle is the curve traced out by the extremity of a line revolving about a point in a plane. It is required to find a straight line equal in length to the

circumference of the circle.   This is easily carried out practically by rolling the circle on a piece of paper until a point on the circumference touching the paper has come back into the plane of the paper.   The distance between the two points is equal to the length of the circumference.

Now suppose a polygon, regular for simplicity, inscribed in the circle, in the manner shown.   If we make the sides of each polygon smaller and smaller, and their number therefore larger and larger, the perimeter of the inscribed polygon increases, while that of the circumscribed
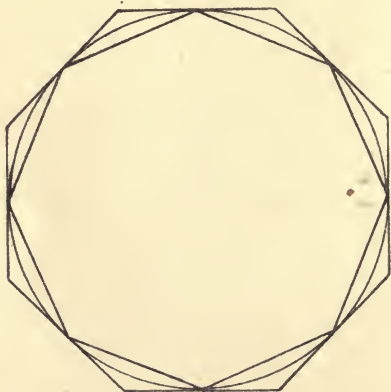
Fig. 4.

polygon decreases.   The two perimeters become more and more nearly equal, and we *define* the limiting value of the perimeter of either polygon, when the number of sides is increased indefinitely, as the *circumference* of the circle.

This is equal to *radius* × 2π, where π is a number which cannot be written exactly as an arithmetical fraction.   Its value can, however, be calculated to as many places of decimals as we please, i.e. to any required degree of approximation.

$$\pi = 3\cdot14159\ldots$$

π is called an *incommensurable number.*

THE RATE OF CHANGE OF A FUNCTION

6. THE FUNDAMENTAL PROBLEM OF THE DIFFERENTIAL CALCULUS

THE conception of the "rate" of change of any magnitude is familiar in many aspects of ordinary experience. The *velocity* of a moving body is the *rate of change of position* of the body. If we consider the body as moving uniformly in a straight line, i.e. describing equal distances in equal intervals of time, its velocity is found by dividing the distance traversed by the time, or

$$v = s/t,$$

where s = distance, say 20 feet,

t = time, say 4 seconds,

v = velocity, $20/4 = 5$ feet *per* second.

The word "per" enters into the specification of a rate.

Now it is the fundamental problem of the Differential Calculus *to find the rate at which one variable changes with regard to another, when the change of the one depends upon the change of the other, and the magnitudes change continuously.*

Two cases at once present themselves:

(i) *The rate of change is constant.* For example in the case of uniform motion the speed does not vary from second to second, and the velocity is found by dividing any distance, however large, by the time taken to traverse that distance.

(ii) *The rate of change is variable.* If a stone be allowed to fall freely under the action of gravity its speed, or rate of change of position, is not constant but increases

by 32 feet per second every second. The distance fallen in t seconds cannot be found by multiplying the velocity of the stone by the time, because that velocity continually increases. It is given by

$$s = \tfrac{1}{2}gt^2,$$

where g is the acceleration of gravity, 32 feet per second per second, i.e. the velocity added on per second. Acceleration is thus the rate of change of velocity.

Let s be the distance fallen after t seconds. After a very small interval δt seconds, the stone has fallen a very small distance δs feet, δt, δs denote small increments of time and space respectively; each is to be taken as a whole, i.e. δt does not mean " t multiplied by δ," but " a small interval of time ". We call δt, δs the *increments* of the variables. The corresponding space and time are now $s + \delta s$ and $t + \delta t$, hence

$$s + \delta s = \tfrac{1}{2}g(t + \delta t)^2,$$
$$\therefore\ s + \delta s = \tfrac{1}{2}gt^2 + gt\delta t + \tfrac{1}{2}g(\delta t)^2.$$
$$\text{But } s = \tfrac{1}{2}gt^2,$$
$$\therefore\ \text{by subtraction, } \delta s = gt\delta t + \tfrac{1}{2}g(\delta t)^2.$$

Dividing by δt we get

$$\frac{\delta s}{\delta t} = gt + \tfrac{1}{2}g\delta t.$$

Now as δt is made smaller and smaller $\delta s/\delta t$ approaches nearer and nearer to the true velocity at the instant t, i.e. the rate at which the stone is falling at the instant t seconds after it is dropped. In the limit, when δt approaches zero,

$$\operatorname{Lim} \frac{\delta s}{\delta t} = gt,$$
$$\delta t \to 0$$

since $\tfrac{1}{2}g\delta t$ is then zero.

Thus the actual velocity at the instant t is gt.

7. THE LAW OF MASS ACTION

It was emphasized by Berthollet that the chemical activity of a substance depends not only upon its *affinity*,

but also on the quantity of it which is available for re-action. He expressed this in the concept of the *active mass* of a substance, and formulated the fundamental law of chemical dynamics, that *the chemical action is proportional to the active mass.* Berthollet did not know exactly how to specify the "active mass" of a substance, and his idea could not take a quantitative form. This formulation appears clearly in the research of Wilhelmy, on the rate of hydrolysis of cane-sugar in the presence of acids. If cane-sugar is heated with a very dilute solution of sulphuric acid, it takes up the elements of water and a molecule of dextrose and one of levulose appear in the place of a molecule of cane-sugar :—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{dextrose}}{C_6H_{12}O_6} + \underset{\text{levulose}}{C_6H_{12}O_6}.$$
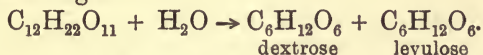
The change is fairly slow, and since a solution of cane-sugar is dextrorotatory (turning the plane of polarized light to the right), and the resulting mixture is levorotatory, the amount of change may be followed by observing the rotation from time to time in a polarimeter.

Let a_0 = rotation of original (cane-sugar) solution,

a_1 = rotation of final (invert-sugar) solution,

a = observed rotation after a time t.

The amount of change is then

$$(\text{original mass of sugar}) \times \frac{a_0 - a}{a_0 - a_1}.$$

The rate of inversion might appear to be given by

$$\frac{\text{amount inverted in time } t}{t},$$

but we have to remember that the rate is a variable one ; the velocity of inversion is, by Berthollet's law, proportional to the active mass of the cane-sugar undergoing change, and hence the velocity *at any instant* is determined by the amount of sugar present *at that instant.* (The water is present in such large excess that its active mass is practically constant.)

Let a = number of gram-molecules of cane-sugar

present at the beginning of the reaction ; a is the *active mass* of the sugar, hence *velocity of reaction at the very beginning* $= ka$, where k is a constant.

If after a time t (usually measured in minutes), an amount x has been inverted, the active mass is then $(a - x)$, and

velocity of reaction at the time $t = k\,(a - x)$.

The velocity slows down continuously as the active mass decreases, just as the velocity of a train slows down as the supply of steam to the cylinders of the engine is gradually cut off. What then is to be understood by the term "velocity of reaction"? The case is analogous to that of a falling stone. Let δx denote the very small quantity of sugar inverted in the very small interval of time δt. Dividing δx by δt we get the *average velocity* of reaction, i.e. the velocity in the interval δt measured on the assumption that this velocity remains constant over that small interval. As a matter of fact it decreases during that interval, owing to the diminution of active mass; but if δt is made smaller and smaller, the change of active mass becomes less and less ; and in the limit, where $\delta t \to 0$, the change of active mass also approaches zero. The ratio $\delta x / \delta t$ approaches a limiting value when δt is continually diminished and this limiting value is defined as *the velocity of the reaction at the time t*. The limiting value of $\delta x / \delta t$ is denoted by $\dfrac{dx}{dt}$, hence

$\text{Lim}\ \dfrac{\delta x}{\delta t} = \dfrac{dx}{dt}$ is the velocity of reaction at time t.

$\delta t \to 0$

Observe that $\dfrac{dx}{dt}$, like δ, is a symbol of operation. It means that we have

(i) Increased t by a small amount δt.

(ii) Divided this into the resulting small change of x, viz. δx.

(iii) Found the limiting value of $\delta x / \delta t$ when $\delta t \to 0$,

It is to be taken as a whole, the dx and dt must not be separated.

Then if at the time t we have $(a - x)$ of cane-sugar present, we may put

$$\frac{dx}{dt} = k\,(a - x)$$

as a quantitative expression of the law of mass action for the reaction considered.

Note that k does not change; it is the factor of proportionality for any active mass, or

$$[\text{velocity}] = k \times [\text{active mass}].$$

Thus the symbols of the Calculus are subject to the same laws and interpretations as those of arithmetic and algebra, but whereas in these parts of the science of number, the numbers are finite and discontinuous, in the Calculus we regard number as being continuous, capable of gradual growth and infinitesimal increase. This idea of the continuity of number, and the conception of limit, closely related to it, are fundamental in the Calculus.

8. DEFINITION OF DIFFERENTIAL COEFFICIENT

$$\text{Let } y = \phi(x) \qquad . \qquad . \qquad . \qquad (1)$$

be a *continuous function* of x.

Let the independent variable x be changed by a very small amount $\pm\, \delta x$, and let $\pm\, \delta y$ be the change of the dependent variable y consequent upon the change. Then we may write

$$y \pm \delta y = \phi(x \pm \delta x),$$
$$\text{hence } \frac{\delta y}{\delta x} = \frac{\phi(x \pm \delta x) - \phi(x)}{\pm\, \delta x}.$$

If *both* the fractions

$$\frac{\phi(x + \delta x) - \phi(x)}{\delta x},$$
$$\frac{\phi(x - \delta x) - \phi(x)}{-\, \delta x}$$

tend to the *same* finite limit as δx is continually decreased, then the function $\phi(x)$ is said to possess a *differential*

coefficient, or a *derived function,* or a *derivative ;* and this
is defined as the value of that limit.

The differential coefficient is denoted by

$$\frac{dy}{dx} = \underset{\delta x \to 0}{\text{Lim}} \frac{\phi(x + \delta x) - \phi(x)}{\delta x} \qquad . \qquad . \qquad (2)$$

Thus dy/dx is *the limiting value of a ratio ;* dy and dx are
not to be regarded as separable quantities because dy/dx
is a symbol denoting a particular operation, namely the
process of finding the limiting value of the $\delta y/\delta x$, where y
and x are connected by the equation

$$y = \phi(x),$$

and δx approaches the value zero.

The importance of the derived function in science
turns upon the point that it measures the *rate of change*
of y with respect to x. This should be remembered when-
ever a differential coefficient is used.

[A function which possesses a differential coefficient, or
a "differentiable" function, is necessarily continuous ; the
converse is not true, because continuous functions having
no differential coefficients are known. These are, however,
very rarely met with in the practical applications of the
calculus ; they are not considered in this book. See Hob-
son, "Theory of Functions of a Real Variable," Cambridge
University Press.]

9. EXAMPLES

The differential coefficients of the following functions
may be obtained *ab initio* :—

(1)
$$y = mx + b,$$
$$y + \delta y = m(x + \delta x) + b,$$
$$\therefore y + \delta y = mx + b + m\delta x.$$

Subtract $y \qquad = mx + b,$

$$\therefore \delta y = m\delta x,$$
$$\therefore \frac{\delta y}{\delta x} = m,$$
$$\therefore \underset{\delta x \to 0}{\text{Lim}} \frac{\delta y}{\delta x} = \frac{dy}{dx} = m.$$

(2) Find the rate of increase of the electrical resistance of a metal wire with temperature from Callendar's formula:—

$$R = R_0(1 + at + bt^2).$$
$$\text{Lim } \frac{\delta R}{\delta t} = \frac{dR}{dt} = R_0(a + 2bt).$$
$$\delta t \to 0$$

This example shows that *time* does not necessarily enter into the specification of a *rate*; we have in this case considered the rate of change of resistance with *temperature*.

(3) Find the rate of increase of pressure with the volume in the case of a perfect gas, at constant temperature.

The functional relation between p and v is Boyle's law:—

$$pv = \text{constant} = K \quad . \quad . \quad . \quad (a)$$

If the volume is *diminished* by a small amount δv the pressure is increased by the small amount δp. The new values of the pressure and volume are $(p + \delta p)$, and $(v - \delta v)$; and since Boyle's law applies to the gas in any state provided the temperature is constant,

$$(p + dp)(v - dv) = K \quad . \quad . \quad (b)$$

From (a) and (b) it follows that $dp/dv = -p/v$.

(4) The area of a circular plate of metal is expanding by heat. When the radius passes through the value 2 in. its length is increasing at the rate of ·01 in. per sec. Show that the area is increasing at the rate of ·04 π sq. in. per sec. at that time. (Area of a circle = πr^2.)

(5) The length of a metal bar at a temperature $t°$ C. is given in terms of the length at 0° C. as unity by the equation

$$l = 1 + at + bt^2.$$

Show that the coefficient of linear expansion is $a + 2bt$.

10. CHEMICAL REACTIONS

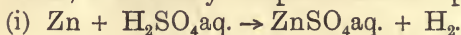When, in any change of a material system, the substances present in the system disappear, and their place

is taken by new substances with different properties, the change is called a *chemical reaction*. If ν_1, ν_2, ν_3, ... molecules of the substances A_1, A_2, A_3, ... are converted into ν_1', ν_2', ν_3', ... molecules of the substances A_1', A_2', A_1', ..., then a *chemical equation* may be written down, expressing, besides the qualitative aspect of the phenomenon, the additional fact that the total mass of the system remains constant, or the sum of the masses of the interacting substances is equal to the sum of the masses of the products of reaction (Law of Lavoisier):—

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \ldots = \nu_1' A_1' + \nu_2' A_2' + \nu_3' A_3' + \ldots$$

If we desire to express the fact that, under specified conditions, the reaction proceeds in a direction from left to right (or vice versa) with respect to the chemical equation, an arrow may conveniently be used instead of the sign " = ," the law of the conservation of total mass being understood

$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightarrow \nu_1' A_1' + \nu_2' A_2' + \ldots$$

Thus, at ordinary temperatures and pressures

(i) $Zn + H_2SO_4aq. \rightarrow ZnSO_4aq. + H_2$.

Here $\nu_1 = \nu_2 = 1$; $\nu_1' = \nu_2' = 1$.

(ii) $Na_2O_2 + 2HClaq. \rightarrow 2NaClaq. + H_2O_2aq.$

$\nu_1 = 1$, $\nu_2 = 2$; $\nu_1' = 2$, $\nu_2' = 1$.

As a first classification we shall say that a reaction is of the *first, second, third, ... n*th, *order*, when one, two, three, ... *n* molecules disappear from the left side of the chemical equation during the reaction.

11. EXAMPLES

(1) *Reactions of the First Order :*—

(*a*) Isomeric change

$$C_6H_5 . CH = NO . OH \rightarrow C_6H_5 . CH_2 . NO_2.$$
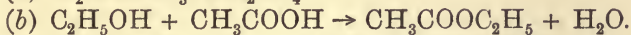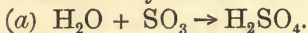
(*b*) Radioactive changes
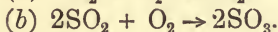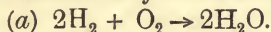
$$Ra, \rightarrow Ra \text{ Emanation}.$$

(*c*) If one reacting component is present in small amount as compared with the other, or others, the amount of the latter converted is negligible compared with the

total quantity present, and the reaction is apparently of the first order with respect to the first component. E.g. the reaction cane-sugar + excess water → invert-sugar is of the first order with respect to cane-sugar.

(2) *Reactions of the Second Order* :—

   (a) $H_2O + SO_3 \rightarrow H_2SO_4$.

   (b) $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$.

   (c) $CH_3COOH + Br_2 \rightarrow CH_2BrCOOH + HBr$.

(3) *Reactions of the Third Order* :—

   (a) $2H_2 + O_2 \rightarrow 2H_2O$.

   (b) $2SO_2 + O_2 \rightarrow 2SO_3$.
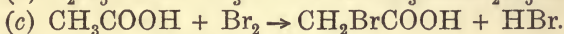
12. VELOCITY OF REACTION

If the substances A_1, A_2, A_3, ... are mixed together, forming either a homogeneous phase, or a heterogeneous system of two or more phases, then three cases arise as to the condition of the system :—

(i) The substances disappear, and new substances appear, so rapidly that the reaction appears to be *instantaneous*. E.g.

$$NaOHaq. + HClaq. \rightarrow NaClaq. + H_2O.$$
$$2H_2 + O_2 \rightarrow 2H_2O \text{ (explosion)}.$$
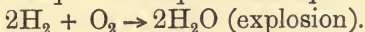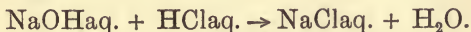
All explosive reactions appear to be instantaneous; careful measurements have shown, however, that the reaction is propagated through the system (gas or liquid) with a finite and characteristic rate, which it is true is very large (Berthelot, Dixon).

(ii) The substances disappear at a finite and measurable rate, which has very different values according to the chemical composition of the reacting system. Examples of such reactions are (1), (a), (b), (c); (2), (b); (3), (b) of the preceding paragraph.

(iii) The initial substances persist without change in quantity for an indefinite time. In this case the composition of the system is independent of the time, and two cases are known :—

3

(a) If, when the amount of one component is changed by any quantity, however small, a corresponding small change in the amounts of one or more of the other components ensues, the state is one of *true equilibrium*. A mixture of acetic acid, alcohol, water, and ethyl acetate in the following proportions satisfies this condition

$$\tfrac{1}{3}CH_3COOH + \tfrac{1}{3}C_2H_5OH + \tfrac{2}{3}CH_3COO\text{Et} + \tfrac{2}{3}H_2O.$$
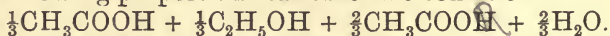
Berthelot found no change in the relative quantities of such a mixture after seventeen years. (It is assumed in all cases, unless otherwise specified, that the *temperature* of the system be kept constant; all reactions are to be conducted isothermally by sinking the reaction vessel in a large mass of water at constant temperature.)

(b) The relative amounts of the components are unchanged if a finite change is made in the amount of one or more of them. Here two cases are possible; either it may be possible to cause the reaction to proceed, at the given temperature, with measurable velocity by the introduction of a so-called *catalyst* into the system; as in the case of a mixture of oxygen and hydrogen gases at ordinary temperature and spongy platinum as catalyst; or a reaction cannot be so instituted, as in the case of metallic gold and oxygen. The first is an example of a system of substances in *false equilibrium;* the second of a system composed of *chemically indifferent* substances. It may be that these distinctions are only arbitrary; all substances may conceivably react, but in some cases the reaction is either much too slow, or proceeds only to such a limited extent, that it is quite imperceptible.

By far the most interesting reactions are those proceeding with a finite and measurable velocity. If the reaction-scheme in such a case be

$$\nu_1A_1 + \nu_2A_2 + \nu_3A_3 + \ldots \rightarrow \nu_1'A_1' + \nu_2'A_2' + \nu_3'A_3' + \ldots$$
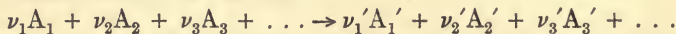
then we shall define the *velocity* of this reaction as the *rate at which the system of the components on the left side is transformed into the system of the components on the right side of the reaction equation.*

13. CHEMICAL KINETICS

The fundamental law of chemical kinetics (that is, that branch of chemistry which deals with the velocities of reactions) is the *Law of Mass Action*, first definitely applied to the problem in hand by Wilhelmy in 1850. This states that *the rate at which a substance disappears from a homogeneous system undergoing chemical change is proportional to the active mass of that substance in the system.*

The *active-mass*, or *concentration*, of a component is taken as the number of gram-molecules per unit volume (usually 1 litre).

A mathematical expression of this law gives us the equations of chemical kinetics.

(1) *Reactions of the First Order* (Unimolecular) :—

Let a = initial amount of $A_1(\nu_1 = 1)$,

x = amount which has disappeared after a time t.

Velocity of reaction = dx/dt,

active mass = $a - x$

$\therefore dx/dt = k_1(a - x)$.

(2) *Reactions of the Second Order* (Bimolecular) :—

Let a = initial amount of $A_1(\nu_1 = 1)$,

b = initial amount of $A_2(\nu_2 = 1)$,

x = amount of A_1 or A_2 disappearing during time t.

Then since the rate of change, dx/dt, is proportional to each active mass, it is proportional to their product, hence

$$dx/dt = k_2(a - x)(b - x).$$

If $a = b$ (case of equal initial concentrations)

$$dx/dt = k_2(a - x)^2.$$

(3) *Reactions of the Third Order* (Termolecular) :—

Let a = initial amount of $A_1(\nu_1 = 1)$,

b = initial amount of $A_2(\nu_2 = 1)$,

c = initial amount of $A_3(\nu_3 = 1)$,
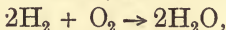
x = amount of A_1, A_2, or A_3 which disappears in time t.

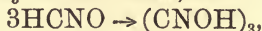Then it is easily seen that
$$dx/dt = k_3(a - x)(b - x)(c - x).$$

The cases for $a = b$, $a = c$, $b = c$, $a = b = c$, should be written out by the student.

If A_1 and A_2 are identical, as in the case
$$2H_2 + O_2 \rightarrow 2H_2O,$$
$\nu_1 = \nu_2$, and $dx/dt = k_3(a - x)^2(c - x)$.

If A_1, A_2, and A_3 are identical, as in the case
$$3HCNO \rightarrow (CNOH)_3,$$
$\nu_1 = \nu_2 = \nu_3$, and $dx/dt = k_3(a - x)^3$.

Generally, if
$$(a - x)/v = c_1,$$
$$(b - x)/v = c_2,$$

where $c_1, c_2, \ldots$ are the actual *concentrations* of the substances $A_1, A_2, A_3, \ldots$ present in the reaction
$$\nu_1 A_1 + \nu_2 A_2 + \ldots \rightarrow \nu_1' A_1' + \nu_2' A_1^2 + \ldots$$
at any particular instant, the rate of change of concentration (obviously negative) is given by
$$- dc_1/dt = kc_1^{\nu_1} c_2^{\nu_2} c_3^{\nu_3}. \ldots$$
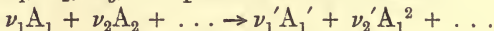
This is the most general equation of chemical kinetics for a reaction proceeding in one direction. If the products of reaction reproduce the initial products, the velocity from left to right is
$$- dc_1/dt = kc_1^{\nu_1} c_2^{\nu_2} \ldots - k' c_1'^{\nu_1'} c_2'^{\nu_2'}. \ldots$$

14. GEOMETRICAL ASPECT OF A DIFFERENTIAL COEFFICIENT; GRADIENT OF A CURVE

The extent to which a road departs from the horizontal per foot of ascent is called the *gradient* or *slope* of the road. In the same way the gradient of a straight line is the increase of y per unit increase of x in the co-ordinate system, that is, the gradient is the trigonometrical tangent of the angle made by the line with the positive direction of the axis of x. In fig. 5,

$$\text{gradient of } \overrightarrow{AB}$$
$$= \delta y/\delta x$$
$$= \tan a.$$

Fig. 5.
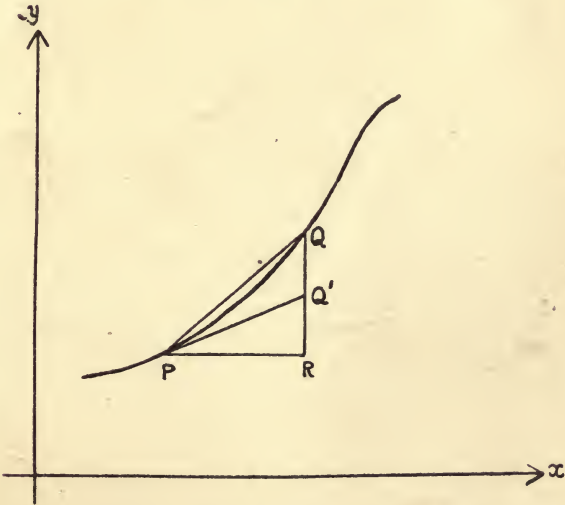
Fig. 6.

If the curve is not a straight line, its gradient varies from point to point along the length of the curve, but it is still possible to speak of the *gradient at any point ;* this being defined as the trigonometrical tangent of the angle made by the positive direction of the x-axis with the tangent line to the curve at the given point, drawn upwards or downwards, towards the right.
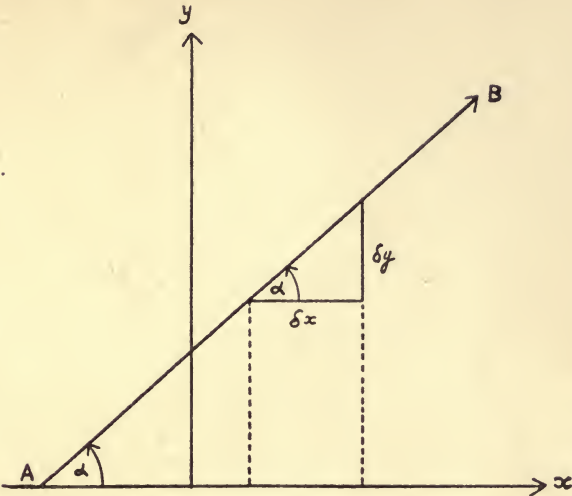
Let PQ be a portion of the curve.   Through P and Q draw PR, QR parallel to the axes, and join PQ.   Let PR = δx, RQ = δy.   Then $\delta y/\delta x = \tan$ QPR is the *slope* or *gradient* of the *secant* PQ.

If the point Q moves along the curve until it coincides with P, the secant becomes the *tangent* PQ′ to the curve at the point P, and $\delta y/\delta x$, since $\delta x \to 0$, becomes dy/dx, which is thus the slope or *gradient of the curve at the point* P.

[*Note.*

P is the point (x, y),
Q is the point $(x + \delta x, y + \delta y)$.]

If ϕ is the angle, positive when measured counterclockwise, which the positive direction of the tangent line makes with the positive direction of the x-axis,

$$dy/dx = \tan \phi.$$

This is an important equation.

It must be noticed that the gradient changes from point to point along the curve, but if the equation of the curve is known the gradient at any point can be calculated. Thus, if the curve is

$$y = 4x^2,$$
$dy/dx = 8x$ ∴ the slope at the point $x = 1, y = 4$ is + 8.   This means that the tangent line to the curve at that point makes an angle with the axis of x the trigonometrical tangent of which is + 8.

15. DIFFERENTIALS

Let $y = \phi(x)$.

Then we have seen that if δy, δx be simultaneous increments of y and x, the limiting value of the ratio $\delta y/\delta x$,

as δx approaches the value 0, measure the rate of change of y with x, and is denoted by

$$\text{Lim} \; \frac{\delta y}{\delta x} = \frac{dy}{dx}.$$
$$\delta x \to 0$$

In another system of notation

$$\text{Lim} \; \frac{\delta \phi(x)}{\delta x} = \frac{d\phi(x)}{dx} = \phi'(x),$$
$$\delta x \to 0$$

where $\phi'(x)$ is called the *Derivative* of y with respect to x. Thus $\frac{dy}{dx}$ and $\phi'(x)$ are two different ways of writing the same thing.

We shall now consider the value of $\delta y/\delta x$ at a point near the limiting value; that is, the change in value of the ratio $\delta y/\delta x$ as δx decreases from a very small finite value to zero.

$$\text{Let } y = x^2$$
$$\delta y = 2x\delta x + (\delta x)^2.$$

If we put $x = 1$, and substitute small numbers for δx, we can form the following table of values:—

δx	$2\delta x$	$(\delta x)^2$	δy
0·1	0·2	0·01	0·21
0·01	0·02	0·0001	0·0201
0·001	0·002	0·000001	0·002001
0·0001	0·0002	0·00000001	0·00020001

We observe that δy becomes more and more nearly equal to $2(\delta x)$ the smaller δx is taken; in other words the importance of the term $(\delta x)^2$ becomes less and less in comparison with $2\delta x$ the nearer δx approaches zero.

Now we can always put

$$\frac{\delta y}{\delta x} = \phi'(x) + \text{R},$$

where R is a quantity which, by the definition of $\phi'(x)$, must vanish in the limit when $\delta x \to 0$. Thus

$$\delta y = \phi'(x)\delta x + \text{R}\delta x.$$

Now as δx approaches the limiting value zero, $R\delta x$ becomes smaller and smaller in comparison with $\phi'(x)\delta x$, since $R = 0$ when $\delta x = 0$. At some point before the limit is actually reached, $R\delta x$ will be so small in comparison with $\phi'(x)\delta x$ that it may be omitted altogether, and we can write

$$dy = \phi'(x)dx,$$

which does not mean that both sides of the equation ultimately vanish, as they should for $\delta x = 0$, but that the *ratio of the two sides approaches unity when δx approaches zero*. In this sense, dy and dx are called *Differentials*. This method, due to Leibnitz, simply means that, in calculations which involve δy and δx, we may, *at any stage*, write $\phi'(x)\delta x$ for δy, omitting terms which ultimately vanish. The full meaning of this statement will become clear as we proceed.

16. GENERAL THEOREMS ON DIFFERENTIATION

The operation of finding the differential of a given function is called *differentiation*. The process is much facilitated by using general rules, which are true for all the functions to be considered.

(1) *The differential of a constant :—*

The rate of change of a constant being zero, it follows that

$$\phi'(k) = 0 \quad \therefore \quad \underline{d(k) = 0.}$$

(2) *The differential of a constant multiplied by a function of x :—*

$$\text{Let } y = ku.$$
$$y + \delta y = k(u + \delta u),$$
$$\therefore \ \delta y = k\delta u,$$
$$\therefore \ \underline{dy = d(ku) = kdu.}$$

(3) *The differential of a sum :—*

$$\text{Let } y = u + v + w + \ldots,$$

where $u, v, w \ldots$ denote different functions of x.

$$y + \delta y = u + \delta u + v + \delta v + w + \delta w + \ldots$$
$$= (u + v + w + \ldots) + (\delta u + \delta v + \delta w + \ldots)$$
$$= y + (\delta u + \delta v + \delta w + \ldots),$$
$$\therefore \ \delta y = \delta u + \delta v + \delta w + \ldots,$$
$$\therefore \ dy = d(u + v + w + \ldots) = du + dv + dw + \ldots$$

(4) *The differential of a product :*—

Let $y = uv$,
$$y + \delta y = (u + \delta u)(v + \delta v),$$
$$= uv + u\delta v + v\delta u + \delta u + \delta u \delta v$$
$$\therefore \ \delta y = u\delta v + v\delta u + \delta u \delta v.$$

Neglecting the term $\delta u \delta v$ which ultimately vanishes, we get

$$dy = d(uv) = u\,dv + v\,du.$$

Similarly

$$d(uvw) = uv\,dw + uw\,dv + vw\,du.$$

(The student must distinguish carefully between cases (2) and (4). In some cases a quantity which is otherwise variable is assumed to be kept constant, and the differentiation must be carried out on this assumption. Thus, in the differentiation of the gas-law

$$pv = \mathrm{RT}$$

we may have the following cases :—

(*a*) p constant (isobar) :—
$$p\,dv = \mathrm{R}d\mathrm{T}.$$
(*b*) T constant (isotherm) :—
$$p\,dv = -v\,dp.$$
(*c*) v constant (isochore) :—
$$v\,dp = \mathrm{R}d\mathrm{T}.)$$

Geometrically, let the long and short sides of the rectangle in fig. 7 be of lengths u and v respectively.

The original rectangle has an area uv. When the sides are increased by δu and δv, the increment of area is the sum of the narrow rectangles $u\delta v$, $v\delta u$, and the small piece $\delta u \delta v$ in the corner. As δu and δv are diminished, it is quite clear that the small corner piece becomes vanish-

ingly small in comparison with the narrow strips, i.e.
$\delta u \delta v$ is negligible in comparison with $u \delta v$ and $v \delta u$.
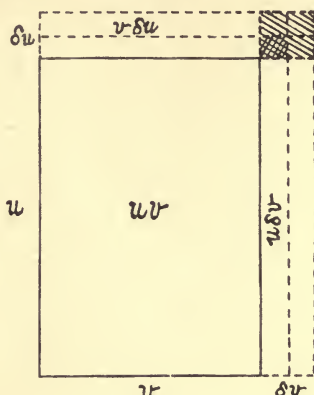
Fig. 7.

(5) *The differential of a quotient :—*

Let $y = \dfrac{u}{v}$,

$$y + \delta y = \frac{u + \delta u}{v + \delta v},$$

$$\delta y = \frac{u + \delta u}{v + \delta v} - \frac{u}{v} = \frac{v \delta u - u \delta v}{v_2 \left(1 + \dfrac{\delta v}{v}\right)}$$

In the limit, $\dfrac{\delta v}{v}$ becomes vanishingly small compared with 1,

$$\therefore \ d\left(\frac{u}{v}\right) = \frac{v\,du - u\,dv}{v^2}. \ \ldots$$

This may be found by putting

$$u = vy$$
$$\therefore \ \delta u = (v + \delta v)(y + \delta y),$$

$$\therefore \ \delta y = \frac{\delta u - y \delta v}{v} = \frac{\delta u - \dfrac{u}{v}\delta v}{v},$$

$$\therefore \ dy = d\left(\frac{u}{v}\right) = \frac{v\,du - u\,dv}{v^2}.$$

The following formulæ contain the results we have just proved; they are constantly used in the further treatment of the subject, and should be committed to memory :—

$$(1) \qquad d(k) = 0.$$

$$(2) \qquad d(ku) = kdu.$$

$$(3) \quad d(u + v) = du + dv.$$

$$(4) \qquad d(uv) = udv + vdu.$$

$$(5) \qquad d\left(\frac{u}{v}\right) = \frac{vdu - udv}{v^2}.$$

THE DIFFERENTIATION OF ALGEBRAIC FUNCTIONS

17. ALGEBRAIC FUNCTIONS AND TRANSCENDENTAL FUNCTIONS

A FUNCTION is said to be *algebraic* when it has been formed by operating on its independent variable according to the laws of algebra, i.e. by addition, subtraction, multiplication, division, involution (formation of powers), or evolution (extraction of roots). Thus: $x + 5$, $x - b$, $x^2 + 5x - 6$, $\sqrt{a^2 - x^2} \sqrt{-3x}$. Functions not algebraic are called *Transcendental Functions*, e.g. $\sin x$, $\tan x$, $\cos^{-1}x$, e^x, $\log x$.

(Compare § 3.)

18. THE DIFFERENTIAL OF x^n

$$\text{Let } y = x^n,$$

and when x is increased to $x_1 = x + \delta x$, let y have the value $y_1 = y + \delta y$.

Then $\dfrac{y_1 - y}{x_1 - x} = \dfrac{x_1{}^n - x^n}{x_1 - x} = x_1{}^{n-1} + xx_1{}^{n-2} + \ldots + x^{n-1}$,

by division. Therefore

$$y - y_1 = (x_1{}^{n-1} + x_1{}^{n-1} + \ldots + x_1{}^{n-1})(x_1 - x).$$
$$\text{But Lim } x_1 = x \text{ by definition of } x_1,$$
$$\delta x \to 0$$
$$\therefore dy = (x^{n-1} + x^{n-1} + \ldots + x^{n-1} + \ldots \text{ to } n \text{ terms}) \, dx$$
$$\text{or } \underline{d(x^n) = nx^{n-1}dx} \qquad . \qquad .$$

It appears, at once, if the equation is written in the form

$$\frac{d(x^n)}{dx} = nx^{n-1},$$

that the gradient of the curve

$$y = x^n$$

is greater the greater the value of n provided $n > 1$. This is evident on comparing the graphs of x^2 and x^3, which are plotted in fig. 8.
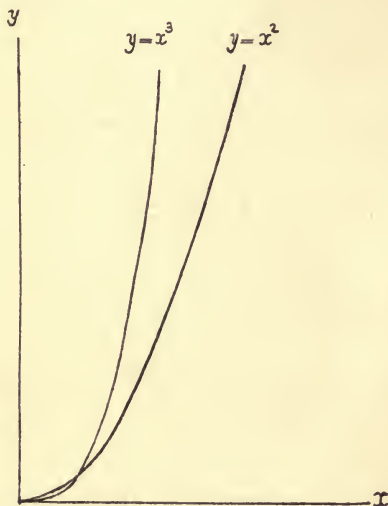
FIG. 8.

19. EXERCISES

Differentiate (find the differentials of) the following functions :—

(1) $y = x^3$.

Working *ab initio* :—

$$y + \delta y = (x + \delta x)^3$$
$$\therefore \ y + \delta y = x^3 + 3x^2\delta x + 3x(\delta x)^2 + (\delta x)^3$$
$$\therefore \qquad \delta y = 3(x^2\delta x + x(\delta x)^2) + (\delta x)^3$$
$$\therefore \qquad dy = d(x^3) = \underline{3x^2dx.}$$

If the formula
$$d(x^n) = nx^{n-1}dx,$$
is used, we must put
$$n = 3 \therefore n - 1 = 2, \text{ and}$$
$$d(x^3) = 3x^2dx, \text{ as before.}$$

(2) x^4, x^9, x^{25}, x^{500}. [$4x^3dx$, $9x^8dx$, $25x^{24}dx$, $500x^{499}dx$.]

(3) $\dfrac{(x+1)(x+2)}{x+3}$.

$$\text{Let } y = \frac{(x+1)(x+2)}{x+3}$$
$$= \frac{x^2 + 3x + 2}{x+3}.$$
$$\text{Put } x^2 + 3x + 2 = u,$$
$$x + 3 = v,$$
$$\therefore y = \frac{u}{v},$$
$$\therefore dy = \frac{vdu - udv}{v^2},$$
$$\therefore dy = \frac{(x+3)(2x+3)dx - (x^2 + 3x + 2)dx}{(x+3)^2},$$
$$\therefore dy = \frac{x^2 + 6x + 7}{x^2 + 6x + 9}dx.$$

(4) Let $y = \dfrac{ax^2 + 2bx + c}{ax^2 - 2bx + c}$.

Put $u = ax^2 + 2bx + c \therefore du = 2(ax + b)dx$;
$v = ax^2 - 2bx + c \therefore dv = 2(ax - b)dx$.

$$\text{But } dy = d\left(\frac{u}{v}\right) = \frac{vdu = udv}{v^2}$$

$$= \frac{2(ax^2 - 2bx + c)(ax + b)dx - 2(ax^2 + bx + c)(ax - b)dx}{(ax^2 - 2bx + c)^2}$$

$$= -2b\frac{(ax^2 - c)}{(ax^2 - 2bx + c)^2}dx.$$

(5) $y = \dfrac{x}{(x+1)(x+2)}$. $\left[dy = \dfrac{-x^2 + 2}{x^2 + 3x + 2}dx \right]$.

(6) $y = \dfrac{x^3 - a^3}{x - a}$.

[Simplify by factorizing the numerator.
$$dy = (2x + a)dx.]$$

(7) $y = (x + 2)^4$.

Put $x + 2 = u$ ∴ $du = dx$.

$$y = u^4 ∴ dy = 4u^3 du$$
$$= 4(x + 2)^3 dx.$$

(8) $y = (x - 5)^9$. $[dy = 9(x - 5)^8 dx]$.

(9) $y = (a - x)^4$. $[dy = -4(a - x)^3 dx]$.

(10) In the adiabatic expansion or compression of a gas, it is found that the pressure and volume are related by the equation

$$pv^\gamma = \text{constant},$$

where $\gamma = C_p/C_v$, the ratio of specific heats. The *elasticity* of a substance under specified conditions being defined as $-v \cdot \dfrac{dp}{dv}$, show that the adiabatic elasticity of a gas is $-\gamma p$.

20. INFINITE SERIES

A collection of terms in which successive terms are related according to some law, is called a *series*. Examples are :—

$$a + (a + m) + (a + 2m) + (a + 3m) + \ldots$$
$$a + ar + ar^2 + ar^3 + \ldots + ar^n.$$

If the number of terms in the series is not finite the series is called an *infinite series*.

Thus $a + ar + ar^2 + \ldots + ar^n + \ldots +$ ad inf. is an infinite geometrical series, in which each term is obtained by multiplying the preceding term by r, the common ratio. If the numerical value of r is less than unity, $|r| < 1$, the sum of an infinite number of terms of the series converges to a finite limit. Let

$$s_{n+1} = a + ar + ar^2 + \ldots + ar^n \text{ to } (n + 1) \text{ terms},$$
$$∴ rs_{n+1} = ar + ar^2 + \ldots + ar^{n+1} \text{ to } (n + 1) \text{ terms},$$
$$∴ s_{n+1}(1 - r) = a - ar^{n+1}$$
$$∴ s_{n+1} = \frac{a(1 - r^{n+1})}{1 - r} = \text{sum of } (n + 1) \text{ terms},$$
$$∴ s_n = \frac{a}{1 - r}(1 - r^n) = \text{sum of } n \text{ terms}.$$

Now let n be continuously increased until it becomes larger than any assignable magnitude, however large; i.e. let $n \to \infty$. Then $r^n \to 0$, since $|r| < 1$ ∴ r^n continuously diminishes as n increases until it becomes smaller than any assignable magnitude, however small, i.e. $r^n \to 0$. Thus

$$s_\infty = \operatorname*{Lim}_{n \to \infty} \frac{a}{1 - r}(1 - r^n) = \frac{a}{1 - r}.$$

Such a series, of which the sum, defined as above, approaches a unique limit, is called a *convergent series*. If the sum does not approach a limit as more and more terms are included, but on the contrary increases without limit, the series is said to be *divergent*. The geometrical series is divergent if $|r| > 1$. A third type of series is the *oscillating* series, such as

$$1 - 1 + 1 - 1 + 1 - \ldots,$$

the sum of which neither converges to a finite limit as the number of terms taken to form the sum is increased, nor diverges under the same circumstance, but oscillates in value :—

$$1 \to 0 \to 1 \to 0 \to \ldots \text{ ad inf.,}$$

the addition of each term causing an increase *per saltum* from 1 to 0 or 0 to 1.

Analytically, we may define a convergent series as follows :—

Let the sum of the first n term of the series be denoted by s_n. Then if s_n approaches a finite and unique limiting value s as n approaches a number which is larger than any assignable magnitude, s is called the *sum* of the convergent series. Let

$$s = s_n + \sigma_n,$$

then the error committed by taking the sum of the first n terms as the sum of the series is

$$s - s_n = \sigma_n.$$

If the series is convergent

$$\operatorname*{Lim}_{n \to \infty} s_n = s, \quad \operatorname*{Lim}_{n \to \infty} \sigma_n = 0.$$

The necessary and sufficient condition for the convergence of an infinite series is that the remainder after n terms, σ_n, becomes infinitely small as n is made very large. There are several methods used for finding whether a given series is convergent or not. Two may be mentioned; for the others the student may consult the text-books on Algebra or the Calculus (Briggs and Bryan, "Tutorial Algebra," pp. 432-9; Lamb, "Calculus," chs. I, XIII.)

Method 1. Let the given series be denoted by

$$u_0 + u_1 + u_2 + \ldots + u_n + \ldots,$$

and let the series

$$v_0 + v_1 + v_2 + \ldots + v_n + \ldots$$

be known to be convergent. Then if each term of the first is not greater than the corresponding term of the second, the first series is convergent. The reference series most frequently used are the geometrical series :—

$$a + ar + ar^2 + \ldots = ar_n + \ldots$$

convergent for $|r| < 1$, and the series :—

$$1 + \frac{1}{2^m} + \frac{1}{3^m} + \frac{1}{4^m} + \ldots$$

convergent if $|m| > 1$.

Method 2. An infinite series is convergent if from and after some fixed term the ratio of each term to the preceding term is numerically less than some quantity which is itself less than unity.

Let the series be

$$a_1 + a_2 + a_3 + \ldots + a_n + \ldots,$$

and let

$$s_n = a_1 + a_2 + \ldots + a_n$$
$$= a_1 \left(1 + \frac{a_2}{a_1} + \frac{a_3}{a_2} \cdot \frac{a_2}{a_1} + \frac{a_4}{a_3} \cdot \frac{a_3}{a_1} + \ldots \right)$$

Then, by hypothesis,

$$a_2/a_1 < a, \ a_3/a_2 < a, \ a_4/a_3 < a, \ \text{etc.},$$

where $a < 1$.

4

Multiplying together the first two, the first three, the first four, and so on, of these inequalities,

$$a_2/a_1 < a \text{ or } a_2 < a \cdot a_1$$
$$a_3/a_1 < a^2 \qquad a_3 < a^2 \cdot a_1$$
$$a_4/a_1 < a^3 \qquad a_4 < a^3 \cdot a_1$$
$$\ldots \qquad \ldots$$

By addition, and adding a_1 to both sides,

$$a_1 + a_2 + a_3 + \ldots < a_1(1 + a + a^2 + \ldots)$$
$$a_1 + a_2 + a_3 + \ldots < a_1/(1 - a).$$

The sum of any number of terms is thus always less than a finite quantity $a_1/(1 - a)$, and the series is convergent.

Examples :—

(1) The series

$$1 + \frac{1}{1} + \frac{1}{2!} + \frac{1}{3!} + \ldots$$

is convergent because, beginning at the mth term

$$a_{m+1}/a_m = 1/m ; \ a_{m+2}/a_{m+1} = 1/m + 1 ;$$
$$a_{m+3}/a_{m+2} = 1/m + 2 \ldots$$

and these quotients are all not greater than a finite quantity $1/m_1$, less than unity.

(2) Show that the series

$$1 + \tfrac{1}{2}x + \tfrac{1}{2} \cdot \tfrac{3}{4}x^2 + \tfrac{1}{2} \cdot \tfrac{3}{4} \cdot \tfrac{5}{6}x^3 + \ldots$$

is convergent when $| x | < 1$.

(3) We will consider two interesting examples of convergent series in chemistry.

(i) *Washing Precipitates.*

R. Bunsen (1868) was the first to try to raise the prosaic operation of washing a precipitate to the rank of a fine art. Suppose the precipitate, say of $AgCl$, is on the filter, and let the concentration of the soluble substance (which is to be washed out) in the original liquid be x_0. E.g. if 250 c.c. of liquid stood over the precipitate, and contained 2·5 gr. HNO_3, the concentration $x_0 = \dfrac{2·5}{250} = 0·01$ gr./c.c.

Let a = volume of liquid left entangled in the precipitate, after as much as possible has drained through, and let

m = volume of liquid poured on for washing.

Total volume of liquid = $m + a$,

$$\therefore \text{ concentration } x_1 = \frac{a}{m + a}x_0.$$

When this liquid has drained through, a c.c. are left in the precipitate. The *absolute* amount of substance left in the precipitate is now $ax_1 = \frac{a}{m + a}ax_0.$

After a second quantity of m c.c. of liquid has been poured on, and drained through, the absolute amount of substance left in the precipitate will be

$$ax_2 = \frac{a}{m + a}ax_1 = \left(\frac{a}{m + a}\right)^2 ax_0.$$

Thus, after 1, 2, 3, ... n washings

$$\frac{a}{m + a}ax_0, \left(\frac{a}{m + a}\right)^2 ax_0, \left(\frac{a}{m + a}\right)^3 ax. \ldots$$

... $\left(\frac{a}{m + a}\right)^n ax_0$ will be the residual quantities left in the precipitate. These terms form a geometrical series with common ratio $a/(m + a)$. If we have a given volume of liquid, V c.c., then V = mn. It is obvious that $\left(\frac{a}{m + a}\right)^n$ will be much smaller if n is large, than when it is small ; it can be shown in fact that it is more efficient to make m fairly small, and n large, than vice versa ; in other words, it is better to wash often with small quantities of liquid than to pour on a large volume at once.

It must be observed that we have assumed that no dissolved substance is retained in the precipitate by *adsorption* ; this condition is, however, very rarely satisfied. (Cf. Freundlich, "Kapillarchemie," Leipzig, 1909.)

(ii) *Extraction with ether, etc.*

Let a solution of aniline in water be shaken out with ether in a separating funnel. Let

a = volume of the aqueous solution,

m = volume of ether added (we assume that none is lost by dissolving in the water, i.e. m is constant),

x_0 = initial concentration of the aniline in the solution. As before let $x_1, x_2, x_3, \ldots x_n$, be the concentrations after $1, 2, 3, \ldots, n$ extractions.

Now it has been shown by Berthelot and Jungfleisch, and by Nernst, that any solute which does not alter its molecular state on passing from one solvent to another, will distribute itself between the two solvents in such a way that the *ratio* of its concentrations in each remains constant, irrespective of the absolute or relative amounts of the two solvents. This ratio is called the *Partition Coefficient* for the particular solute and pair of solvents; let it be denoted by ω. Then

$$\frac{\text{concentration in water}}{\text{concentration in ether}} = \text{constant} = \omega,$$

$$\therefore \frac{x_1}{a} = \omega\frac{x_0 - x_1}{m},$$

$$\therefore x_1 = \frac{\omega a}{m + \omega a}x_0.$$

A second, third, . . . nth extraction gives

$$\frac{x_2}{a} = \omega\frac{x_1 - x_2}{m}$$

$$\therefore x_2 = x_0\left(\frac{\omega a}{m + \omega a}\right)^2,$$

$$x_3 = x_0\left(\frac{\omega a}{m + \omega a}\right)^3,$$

$$\cdots$$

$$x_n = x_0\left(\frac{\omega a}{m + \omega a}\right)^n.$$

Complete extraction is theoretically impossible, because $\left(\frac{\omega a}{m + \omega a}\right)^n$, although it may become very small, is never zero. The number of extractions (n) requisite to reduce the concentration in the aqueous layer to a small

value, will depend on the magnitude of ω.   In the case of ether and water,

> $\omega = 1/80$ for benzoic acid, i.e. eighty times as much goes into the ether as into the water.   If $a = 1000$, $m = 200$, then

$$\frac{x_1}{x_0} = \frac{\omega a}{m + \omega a} = \frac{1}{17},$$

i.e. after one extraction only $1/17$ of the acid is left in the water.   After three extractions, only $(\frac{1}{17})^3 = 1/4913$ is left, and the extraction is "complete".   For succinic acid, with the same solvents, $\omega = 6$.   After one extraction $\frac{30}{31}$ is left; repeated extraction is necessary.

21. THE BINOMIAL SERIES

The Binomial Series, discovered by Newton, is of very frequent use in scientific investigation :—

$$(1 + x)^n = 1 + nx + \frac{n(n - 1)}{1 \cdot 2}x^2 + \frac{n(n - 1)(n - 2)}{1 \cdot 2 \cdot 3}x^3$$
$$+ \ldots + x^n.$$

(a) If n is *positive* and *greater than unity*, the expansion holds good for all values of x.
Thus

$$(1 + x)^5 = 1 + 5x + \frac{5 \cdot 4}{1 \cdot 2}x^2 + \frac{5 \cdot 4 \cdot 3}{1 \cdot 2 \cdot 3}x^3 + \frac{5 \cdot 4 \cdot 3 \cdot 2}{1 \cdot 2 \cdot 3 \cdot 4}x^4 + x^5.$$

If the first term in the binomial is not unity, it can be made unity by division :—

$$(a + x)^4 = \left(1 + \frac{x}{a}\right)^4 a^4 = a^4\left(1 + 4\frac{x}{a} + 6\frac{x^2}{a^2} + \ldots\right)$$

Examples.—Find the expansions of the following binomials, testing the resulting series by giving x a numerical value :—

> (1) $(1 + 2x)^3$.
> (2) $(1 - 4x)^4$.
> (3) $(a + x^2)^3$.

(b) If n is *fractional* or *negative*, the series is convergent provided the *numerical* value of x is less than unity,

i.e. $-1 < |x| < +1$. This condition can always be satisfied if the second term in the binomial is an infinitesimal, $(1 + \delta x)$, because we can always suppose δx to be less than unity before the expansion is made.

Examples :—

(1) Expand $(8 + x)1\frac{1}{3}$

$$(8 + x)^{1\frac{1}{3}} = \left\{8\left(1 + \frac{x}{8}\right)\right\}^{1\frac{1}{3}} = 8^{1\frac{1}{3}}\left(1 + \frac{x}{8}\right)^{1\frac{1}{3}}$$

$$= 16\left\{1 + 1\frac{1}{3}\cdot\frac{x}{8} + \frac{1\frac{1}{3}(1\frac{1}{3} - 1)}{1\cdot 2}\cdot\left(\frac{x}{8}\right)^2\cdot\right.$$

$$+ \frac{1\frac{1}{3}(1\frac{1}{3} - 1)(1\frac{1}{3} - 2)}{1\cdot 2\cdot 3}\left(\frac{x}{8}\right)^3 + \left.\ldots\right\}$$

$$= 16 + 2\frac{2}{3}x + \frac{1}{18}x^2 - \frac{1}{648}x^3, \text{ etc.}$$

(2) Find the cube-root of $(x + 4)^4$ to four terms.

(3) Expand $(1 - x)^{-1}\cdot[1 + x + x^2 + x^3 + \ldots]$.

(4) Expand $(1 - x)^{-3}\cdot[1 + 3x + 6x^2 + 10x^3 + \ldots]$.

(5) Prove that $d(x^n) = nx^{n-1}dx$, by using the Binomial Series. Since the binomial expansion can be used for positive and negative, integral and fractional values of n, the formula for the differentiation applies to all these cases.

MAXIMUM AND MINIMUM VALUES OF A FUNCTION

22. MAXIMA AND MINIMA

CONSIDER the curve in fig. 9.   Notice the sign of the gradient as the tangent line rolls round the crest A and the trough B.
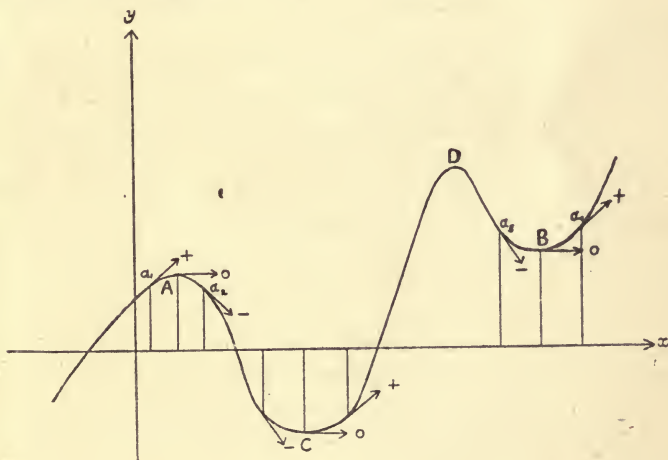
Fig. 9.

At a_1 the tangent line makes a positive angle with the x-axis

$$\therefore \tan \phi = dy/dx \text{ is } \textit{positive.}$$

At A the tangent line is parallel to the x-axis

$$\therefore \tan \phi = dy/dx \text{ is } \textit{zero.}$$

At a_2 the tangent line makes a negative angle with the x-axis

$$\therefore \tan \phi = dy/dx \text{ is } negative.$$

The changes of sign as the tangent line rolls round a crest are in the order

$$[+] \rightarrow [0] \rightarrow [-].$$

At B, the trough, the changes are in the order

$$[-] \rightarrow [0] \rightarrow [+].$$

Definition : a *maximum* value of a function is a value algebraically greater than all values *in the immediate neighbourhood.*

The points A, D, on the graph thus satisfy the condition for maxima.

Definition : a *minimum* value of a function is a value algebraically less than all values *in the immediate neighbourhood.*

The points B, C, on the graph satisfy the condition for minima. The case of C will repay close attention.

Notice that a maximum value need not be the greatest value of the function ; this may be one maximum value, e.g. D, but the criterion refers only to values in the immediate neighbourhood of the point considered. Similarly for minimum values. This explains why a function may have more than one maximum (or minimum) value.

The elementary methods of finding the maximum and minimum values of a function depend upon the properties of quadratic equations ; they are discussed in all text-books on algebra. Far more rapid and simple is the method of the Calculus, which follows at once from the foregoing remarks.

At a *maximum*, dy/dx passes from a positive, through zero, to a negative value.

At a *minimum*, dy/dx passes from a negative, through zero, to a positive value.

The maxima and minima are therefore to be determined by the changes of sign of the gradient at the critical points. It is important to notice that dy/dx vanishes for *both* a

maximum and a minimum; the changes of sign determine which case is under investigation.

Examples :—

(1) Find the maximum or minimum values of the function $3x^2 + 2x - 6$.

[*Solution :* Put $y = 3x^2 + 2x - 6$.

$$\frac{dy}{dx} = 6x + 2.$$

For a maximum or minimum, $\frac{dy}{dx} = 0$,

$$\therefore\ 6x + 2 = 0,$$
$$\therefore\ x = -\tfrac{1}{3} = -0.33\ldots.$$

Substitute values a little less, and a little greater, than 0.33 and observe the change of sign.

(i) $x = -0.2$

$$\therefore\ dy/dx = -(6 \times 0.2) + 2 = +0.8.$$

(ii) $x = -0.4$

$$\therefore\ dy/dx = -(6 \times 0.4) + 2 = -0.4.$$

Consequently the changes of sign are

$$(\overset{\bullet}{-}) \to (0) \to (+),$$

and we are dealing with a *minimum*.

(Notice that -0.4 is algebraically less than -0.2.)]

This result should be confirmed by plotting the graph of $3x^2 + 2x - 6$.

(2) Find the maxima, or minima, of

$$4x^3 - 10x^2 + 3x + 7.$$

[Put $y = 4x^3 - 10x^2 + 3x + 7$

$$\therefore\ dy/dx = 12x^2 - 20x + 3.$$

For maxima or minima

$$dy/dx = 12x^2 - 20x + 3 = 0,$$
$$\therefore\ x = \tfrac{3}{2} \text{ or } \tfrac{1}{6}.$$

Take the values separately :—

(a) $x = 3/2 = 1.5$.

(i) Put $x = 1.4$, dy/dx is $-$,

(ii) Put $x = 1.6$, dy/dx is $+$,

$\therefore$ we have the $- \to 0 \to +$ case,

i.e. a *minimum* at $x = 1.5$,

(b) $x = 1/6 = 0.166$.

 (i) Put $x = 0.10$, dy/dx is $+$,
 (ii) Put $x = 0.2$, dy/dx is $-$,

$\therefore$ we have the $+ \to 0 \to -$ case,

i.e. a *maximum* at $x = 0.1\dot{6}$.]

(3) Find the maximum and minimum values of

$$x(x - 1)^2$$

[There is a maximum at $x = \frac{1}{3}$, a minimum at $x = 1$. The corresponding values of the function, obtained by substitution, are $\frac{4}{27}$, 0.]

(4) Find the points on the curve

$$y = (x - 1)^2(x - 2)^2$$

which are at maxima or minima.

 [$dy/dx = 2(2x^3 - 9x^2 + 13x - 6)$.

This can be factorized by making use of the *Factor Theorem*: "If a rational integral algebraic expression vanishes when a is put for x, then $(x - a)$ is a factor".

The above vanishes for $x = + 1, + 2, + \frac{3}{2}$

 $\therefore$ $(x - 1)$, $(x - 2)$, $(2x - 3)$ are factors.
 $dy/dx = (x - 1)(x - 2)(2x - 3) = 0$
 $\therefore$ $x = 1, 2$ or $\frac{3}{2}$.

As x passes through the value $+ 1$, $\dfrac{dy}{dx}$ changes from $-$ to $+$

,, ,, ,, $+ 2$, ,, ,, $-$,, $+$
,, ,, ,, $+ \frac{3}{2}$, ,, ,, $+$,, $-$

Evaluating corresponding y-values we find,

 a *maximum* at $(\frac{3}{2}, \frac{1}{16})$,
  minima at $(1, 0)$. and $(2, 0)$.]

(5) $y = \dfrac{x^2 - x + 1}{x^2 + x + 1}$.

 [A minimum at $(1, \frac{1}{3})$; a maximum at $(- 1, \frac{1}{3})$.]

(6) $x^4 - 8ax^3 + 22a^2x^2 - 24a^3x + 12a^4$.

 [$x = a$(a min.); $x = 2a$(a max.); $x = 3a$(a min.)]

(7) $(x - 1)^4(x + 2)^3$.

 [$x = 1$ (a min.); $x = - \frac{5}{7}$ (a max.)]

(8) $\dfrac{x^3 + 1}{x^2}$. [$x = \sqrt[3]{2} = 1.26, \ldots$ (a min.)]

23. CALCULATION OF SMALL ERRORS

Let some variable x, on which another variable y depends, be measured in the laboratory. It is required to find what effect a small error in the measurement of x would have upon the value of y. We use the equation

$$dy = \phi'(x)dx,$$

i.e. an error of dx in x causes an error $\phi'(x)dx$ in y. This is called the *absolute error*.
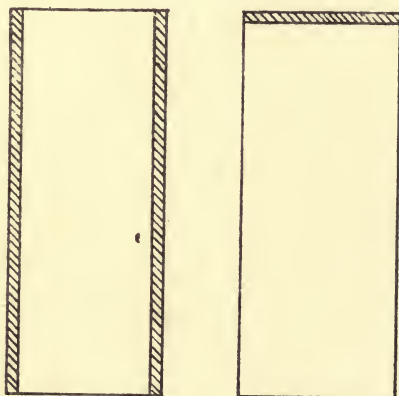
FIG. 10.—Radius Error.   Height Error.

Examples :—

(1) In measuring a cylinder, a possible error of dr is made in the radius. What is the error in the estimate of the volume?

$$v = \pi r^2 h$$
$$\therefore dv = 2\pi r h\, dr,$$

i.e. the error dr is multiplied by $2\pi r h$.

If $h = 7$ cm., $r = 1$ cm., $dr = \mp 0.01$ cm.

$$dv = 2.2 \text{ c.c.} - \text{an appreciable amount.}$$

Hence one has to be very careful indeed in measuring the radius,

The effect of an equal error in measuring the height is

$$dv = \pi r^2 dh$$
$$= 3\cdot14 \times 1 \times \cdot01 = \cdot03 \text{ c.c.,}$$

which is negligible.

(2) The curious divergencies of students' results from the "theoretical" values are often explained by the fact that some quantity has not been measured with sufficient accuracy; the accuracy which is sufficient for some portion of the work is not sufficient for others.

Thus, if the coefficient of linear expansion of a metal bar is to be found, the formula is

$$l = l_0(1 + at).$$

If $l_0 = 100$ cm., $t = 100°$, an error of 0·1 cm. in l_0 will make an inappreciable difference in a.

But $a = (l - l_0)/l_0 t = \varDelta l/l_0 t$
$\therefore da = d(\varDelta l)/l_0 t.$

For an error of 0·1 cm. in $\varDelta l$ (the increase of length), an error of 0·00001 cm. is made in a, and since, for iron, $a = 0\cdot000013$, this would give a totally incorrect result.

This example shows that the accuracy required in the measurement depends not only on the form of the function connecting the variables, but also on the absolute magnitude of the quantity to be found. It is therefore usual to find the *proportional error*, that is, to divide the absolute error by the value of the quantity, or da/a. This, multiplied by 100, is the *percentage error*.

(3) Very often a suitable arrangement of the conditions of experiment reduces the error to a minimum. It is shown in the text-books on practical electricity that the minimum error is made in measuring a current with a tangent galvanometer when the deflection is 45°, other sources of error being neglected. The current through the instrument is therefore adjusted by shunting until this deflection is approximately obtained.

(4) If there are errors in more than one variable, the error for each is calculated separately and the results added. ("Superposition of Small Errors.") If the density

of a body is to be found by Archimedes' method, and if the weights in air and in water are in error by $d\mathrm{W}$, $d\mathrm{W}^1$, show that the relative error in the density ρ will be

$$d\rho/\rho = -\frac{\mathrm{W}^1}{\mathrm{W} - \mathrm{W}^1}\frac{d\mathrm{W}}{\mathrm{W}} + \frac{d\mathrm{W}^1}{\mathrm{W} - \mathrm{W}^1}$$

24. EXAMPLES

If $y = f(x)$,

then it has been shown that

$$\delta y = y + \delta y - y = f(x + \delta x) - f(x),$$

and if δx is *small* (otherwise the experimental results are useless)

$$f(x + \delta x) - f(x) = f'(x)\delta x$$
$$\therefore \textit{absolute error} = \delta y = f'(x)\delta x,$$
$$\text{and } \textit{relative error} = \delta y/y = \frac{f'(x)}{f(x)}\delta x.$$

(a) *Atomic weight determinations* :—

Let the equivalent of sodium be determined by precipitating a known weight x of NaCl with 1 part of Ag, and weighing the AgCl.

Let A = equivalent of silver

B = equivalent of chlorine,

both be known. Then if y is the equivalent of Na,

$$(y + \mathrm{B}) : \mathrm{A} = x : 1,$$
$$\therefore \ y = \mathrm{A}x - \mathrm{B},$$
$$\therefore \ \delta y = \frac{f'(x)}{f(x)}\delta x = \frac{\mathrm{A}}{\mathrm{A}x - \mathrm{B}}\ \delta x,$$
$$= \frac{\mathrm{A}}{y}\delta x = \frac{y + \mathrm{B}}{y}\cdot\frac{\delta x}{x},$$
$$= \frac{23 + 35{\cdot}5}{23}\cdot\frac{\delta x}{x}.$$

An error of 0·1 parts in a thousand in the measurement of x gives rise to an error of 0·25 parts per thousand in the calculated value of y. In the case of $\mathrm{BaCl_2}$, $y = 137/3$,

$$\frac{y + \mathrm{B}}{y} = 1{\cdot}52.$$

(b) *Reaction velocity :*—

The constant k in the formula

$$dx/dt = k(a - x)(b - x) \dots$$

will be shown later on to be given by

$$k = \frac{1}{t}\phi(x),$$

$$\text{or } y = \frac{1}{t}\phi(x),$$

where $y = k$; $\phi(x)$ is a function of x.

A small error in the measurement of t has very little influence on y ; an error in the estimation of x (the extent of reaction) on the contrary, gives rise to a marked error.

$$\delta y = \frac{1}{t}\phi'(x)\delta x.$$

(c) In a series of determinations, the values of δx are usually nearly equal, hence the errors in y are proportional to $\phi'(x)/t$. The *reliability* of any calculated value of y is therefore proportional to $t/\phi^1(x)$. The best value of y is in this case found by multiplying each calculated value by the corresponding value of $t/\phi^1(x)$, and dividing the sum of these products by the sum of the latter expressions :—

$$y = \frac{y_1 \dfrac{t_1}{\phi'(x_1)} + y_2 \dfrac{t_2}{\phi'(x_2)} + \dots}{\dfrac{t_1}{\phi'(x_1)} + \dfrac{t_2}{\phi'(x_2)} + \dots}$$

$t_1/\phi'(x_1)$ is called the *weight* of the observation (1).

The relative error,

$$\frac{\delta y}{y} = \frac{1}{t} \cdot \frac{\phi'(x)}{\phi(x)}\delta x,$$

diminishes with diminishing values of δx and $\dfrac{\phi'(x)}{\phi(x)}$.

The experimental conditions are therefore to be arranged so that $\phi'(x)/\phi(x)$ is *a minimum*.

This is the case when

$$\frac{d}{dx}\left(\frac{\phi'(x)}{\phi(x)}\right) = \left(\frac{\phi'(x)}{\phi(x)}\right)' = 0.$$

Thus, in the measurement of conductivity by Kohlrauch's method, the error is least in the bridge-reading when the slider is in the neighbourhood of the middle of the stretched wire.

Let y = resistance measured (i.e. of the electrolyte),

l = length of wire,

x = reading when the bridge is balanced.

$$\text{Then } y = f(x) = w\frac{l}{l - x},$$

where w = ratio of the resistances in the " ratio-arms " of the bridge.

$$\frac{f'(x)}{f(x)} = \frac{l}{x(l - x)},$$

$$\therefore \left(\frac{f'(x)}{f(x)}\right)' = l\frac{2x - l}{x^2(l - x)^2}.$$

This vanishes for $(2x - l) = 0$, or $x = l/2$.

If the scale, the ratio of the resistances in the ratio-arms, and the reading x are all affected by errors, the relative error in the calculated resistance will, by the principle of superposition of separate small errors, be

$$\frac{\delta y}{y} = \frac{l}{x(l - x)}\delta x + \frac{1}{w}\delta w - \frac{1}{l - x}\delta l.$$

25. DIFFERENTIATION OF A FUNCTION OF A FUNCTION

If we were asked to differentiate $\sqrt{1 + x^2}$, it might appear at first sight that the formula

$$d(x^n) = nx^{n - 1}dx$$

would apply, and we should have

$$d(\sqrt{1 + x^2}) = d(1 + x^2)^{\frac{1}{2}} = \tfrac{1}{2}(1 + x^2)^{-\frac{1}{2}}dx. \qquad \text{(i)}$$

This is *not* the case, because $\sqrt{1 + x^2}$ is a function not of x simply, but of x^2.

Let us write u for $1 + x^2$, then

$$\sqrt{1 + x^2} = u^{\frac{1}{2}},$$

$$d(\sqrt{1 + x^2}) = d(u^{\frac{1}{2}}) = \tfrac{1}{2}u^{-\frac{1}{2}}du. \qquad \text{(ii)}$$

We can see at once where the error comes into statement (i), because du is not equal to dx unless $u = x$. In

this case it is evident that the addition of a constant to x does not affect the form of the result :—

$$d(1 + x)^2 = 2(1 + x)dx.$$

But in the example we are considering, $u = 1 + x^2$ $\therefore du = 2xdx$, hence the complete result is

$$d(\sqrt{1 + x^2}) = \tfrac{1}{2}u^{-\tfrac{1}{2}}du = \tfrac{1}{2} \cdot \frac{1}{\sqrt{1 + x^2}} \cdot 2xdx,$$

$$\therefore d(\sqrt{1 + x^2}) = \frac{x}{\sqrt{1 + x^2}}dx.$$

Similarly, $d(\sqrt{1 - x^2}) = -\dfrac{x}{\sqrt{1 - x^2}}dx.$

Generally, if the function to be differentiated is a *function of a function* of x, we put the function of x equal to u, and proceed in the usual way, taking care not to omit to find du and substitute in the final result.

Example.—Differentiate $\sqrt{a^2 + x^2}$.

$$\text{Let } a^2 + x^2 = u,$$
$$\therefore \sqrt{a^2 + x^2} = u^{\tfrac{1}{2}}$$
$$\therefore d(\sqrt{a^2 + x^2}) = \tfrac{1}{2}u^{-\tfrac{1}{2}}du.$$
$$\text{But } du = d(a^2 + x^2) = 2xdx,$$
$$\therefore d(\sqrt{a^2 + x^2}) = \frac{x}{\sqrt{a^2 + x^2}}dx.$$

In general symbols let

$$y = \phi(u),$$
$$\text{where } u = f(x).$$
$$d[\phi(x)] = \phi'(x)dx, \text{ by definition,}$$
$$\therefore d[\phi(u)] = \phi'(u)du.$$
$$\text{But } du = d[f(x)] = f'(x)dx,$$
$$\therefore dy = \phi'(x) \cdot f'(x)dx.$$

Thus to differentiate a function of a function of x, we multiply the differential coefficient of the original function, taken as a whole, by the differential of that function with respect to x.

26. EXAMPLES

Differentiate the following expressions with respect to x :—

(1) $\sqrt{a^2 - x^2}$. $\left[-\dfrac{x}{\sqrt{a^2 - x^2}}dx \right]$.

(2) $\sqrt[3]{a^2 + x^2}$. $[\frac{2}{3}(a^2 + x^2)^{-\frac{1}{3}}x dx]$.

(3) $(ax + b)^n$. $[an(ax + b)^{n-1}dx]$.

(4) $\sqrt{\dfrac{1 + x + x^2}{1 - x + x^2}}$. [Hint: Put $1 + x + x^2 = u$,

$1 - x + x^2 = v$, and use the
formula for a quotient. The result is

$$\frac{1 - x^2}{(1 + x + x^2)^{\frac{1}{2}}(1 - x + x^2)^{\frac{3}{2}}}dx.]$$

(5) Find the elasticity of a gas obeying van der Waals'
equation :—

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{constant}.$$

[The equation, when multiplied out, becomes

$$pv - bp + \frac{a}{v} - \frac{ab}{v^2} = \text{constant},$$

$$\therefore pdv + vdp - bdp - \frac{a}{v^2}dv - 2\frac{ab}{v^3}dv = 0$$

$$\therefore \frac{dp}{dv}.v = \text{elasticity} = -\left(p - \frac{a}{v^2} + \frac{2ab}{v^3}\right).\frac{v}{v - b}\right].$$

(6) The velocity of a compressional wave through an
elastic fluid is given by Newton's formula

$$\text{velocity} = u = \sqrt{\frac{e}{\rho}}, \text{ where}$$

e = elasticity of the fluid under the conditions obtaining
when the wave is passing, ρ = density of the uncompressed
fluid.

Show that for a change of density $d\rho$, the change of
elasticity is $-\frac{1}{2}\sqrt{e}.\dfrac{d\rho}{\sqrt{\rho^3}}$.

If the fluid is a gas obeying Boyle's law, $e = \gamma p$, $\rho = 1/v$
where v = volume of unit mass, because the conditions
obtaining when the sound wave passes are adiabatic con-
ditions, and we have shown that the adiabatic elasticity
is ($\rho \times$ pressure),

5

Thus $u = \sqrt{\gamma pv}$.

Show that $du/dp = 0$, i.e. the velocity is independent of the pressure. [$v = k/p$ by Boyle's law.]

(7) Differentiate $(ax^n + c) \cdot {}^m[m(ax^n + c)^{m-1}nax^{n-1}dx]$.

(8) Differentiate $(a + bx^3)^2(a - x)^{\frac{3}{2}}$. [Hint:

Put $y = uv = (a + bx^3)^2 \times (a - x)^{\frac{3}{2}}$.

$$dy = (a + bx^3)(a - x)^{\frac{1}{2}} \cdot \frac{12abx^2 - 15bx^3 - 3a}{2}dx \bigg].$$

(9) Differentiate $\dfrac{(x + 3)^3}{(x^2 - 2)^2} \cdot \left[\dfrac{(x+3)^2 \cdot (-x^2 - 12x - 6)}{(x^2 - 2)^3}dx\right]$.

(10) If $y = \mathrm{F}(ax^n \pm b)$ show that
$$dy = an\mathrm{F}'(ax^n \pm b)x^{n-1}dx.$$

(11) If $y = \{\mathrm{F}(x)\}^n$ prove that
$$dy = n\{\mathrm{F}(x)\}^{n-1} \times \mathrm{F}'(x)dx.$$

Compare with examples (7) and (8).

27. EXAMPLES ON MAXIMA AND MINIMA

If a given function
$$y = \phi(x)$$
is to have a maximum or a minimum value, it is necessary but not sufficient that x shall have a value which satisfies the equation
$$\frac{dy}{dx} = \phi'(x) = 0.$$

The condition which must at the same time be satisfied in order that the function shall be a maximum or a minimum is that $\phi'(x)$ shall change sign as x passes through the value which makes $\phi'(x)$ vanish. The criterion for a maximum or a minimum is found in this change of sign of the function as x increases from a value, a little less than the critical value ($\phi'(x) = 0$), to a value a little greater.

For a *maximum*, the change of sign is $(+) \to (0) \to (-)$.

For a *minimum*, the change of sign is $(-) \to (0) \to (+)$.

If $\phi'(x)$ does *not* change sign in passing through zero, that is, if the criterion becomes
$$(+) \to (0) \to (+),$$
$$\text{or } (-) \to (0) \to (-),$$

the curve becomes parallel to the axis at that point, but then continues in the same direction as at first.

Let acb be a line parallel to the x-axis and cutting a curve in three points a, c, b. If the three points approach and ultimately coincide, we have a point satisfying the condition given above. At this point (such as P) there is a sudden change of direction; it is therefore called a *point of inflection*. The critical point on the critical isotherm of van der Waals' equation is an example of such a point.
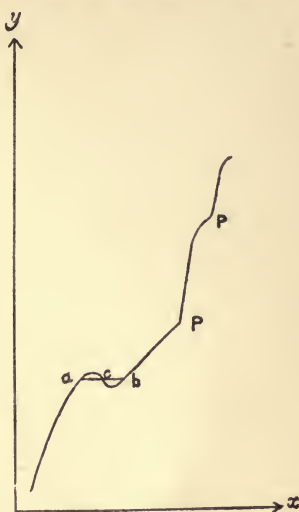
FIG. 11.

Examples.—Find the maximum or minimum values of

(1) $2x^3 - 3x^2 - 36x + 10$.

[Max. at $= x - 2$, min. at $x = 3$.]

(2) $4x^3 - 18x^2 + 27x - 7$.

[Point of inflexion at $x = 1\cdot5$.]

(3) $x\sqrt{ax - x^2}$.   [Max. at $x = 3a/4$.]

(4) $\dfrac{x(x^2 + 1)}{x^4 - x^2 + 1}$.   [Max. value is $+ 2$, min. value $- 2$.]

(5) $\dfrac{x(x^2 - 1)}{x^4 - x^2 + 1}$.

[2 max. values of $+ 0\cdot5$, 2 minima of $- 0\cdot5$.]

(6) In deep water, a wave of length λ is propagated with a velocity

$$u = \sqrt{\frac{\lambda}{a} - \frac{a}{\lambda}},$$

where a is a constant.

Show that the wave-length for maximum velocity is $\lambda = a$.

(7) The magnetic force on a small magnet placed at some point on a line drawn through the centre of a circular coil, and perpendicular to the plane of the coil is

$$F = k\frac{x}{(a^2 + x^2)^{\frac{5}{2}}},$$

where x = distance of magnetic pole from plane of coil,
a = radius of coil.

This is a maximum when $x = \frac{1}{2}a$.

(8) If methyl acetate is hydrolysed in presence of acetic acid as catalyst, the acetic acid produced increases the concentration of catalyst as the reaction progresses:—

$$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH.$$
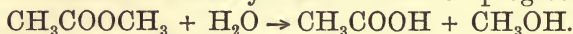
From this cause alone the velocity would increase with time; but since the active mass of ester diminishes, the velocity from this latter cause would decrease. At some point the velocity, after increasing, will have a maximum value. It then begins to decrease. When is the velocity a maximum? Start with a of acetic acid, b of methyl acetate, and after a time t let x be hydrolysed, producing n molecules of acetic acid.

Velocity due to acetic acid added = $\dfrac{dx_1}{dt} = k_1a(b - x)$,

Velocity due to acetic acid produced = $\dfrac{dx_2}{dt} = k_1x(b - x)$,

∴ actual velocity = sum of component velocities, or

$$\frac{dx}{dt} = \frac{dx_1}{dt} + \frac{dx_2}{dt} = k_1(a + x)(b - x).$$

For a *maximum*, $\dfrac{d}{dt}\left(\dfrac{dx}{dt}\right) = 0$

$$\therefore \frac{d}{dt}(a + x)(b - x) = 0$$

$$\text{or} - (a - b) = 2x = 0$$

$$\therefore x = \tfrac{1}{2}(a - b).$$

Ostwald calls such reactions *autocatalytic*.

Observe that we have differentiated a differential coefficient. The result, representing the rate of change of a

velocity, or an *acceleration*, is called the *second differential coefficient* with respect to *t*. It is written $\frac{d^2x}{dt^2}$, or $\phi''(t)$. Curves representing the amount of changing *substance*, *x*, as a function of the time, are called *velocity curves*. Curves representing the *velocity* or rate of change of active mass, as a function of the time, are called *acceleration curves*.

Since dy/dx measures the *gradient* of the curve $y = \phi(x)$, d^2y/dx^2 will measure the *rate of change of the*

gradient. We can illustrate the meaning of this expression by considering the two roads represented in section in fig. 12. The gradients at points equidistant from the starting-points are obviously greater in the second case than in the first, or the gradient is increasing at a greater rate. Thus d^2y/dx^2 is greater along the curve AB′ than along AB.

As we should say, the road AB′ gets steeper much more rapidly than the road AB. d^2y/dx^2 is thus a measure of the rate at which the gradient is increasing.

EXPONENTIAL AND LOGARITHMIC FUNCTIONS

28. INDICES

IN elementary algebra, a^m is defined as the product of m factors, each equal to a :—

(1) $a^m = a \times a \times a \ldots$ to m factors.

a is any positive or negative, integral or fractional, quantity.

The *index* m is a positive integer, otherwise the expression is meaningless. From the definition it is easy to show that, if m and n are positive integers :—

(2) $a^m \times a^n = a^{m+n}$
(3) $a^m/a^n = a^{m-n}$, if $m > n$,
$\quad = 1/a^{n-m}$, if $m < n$.
(4) $(a^m)^n = a^{mn}$.
(5) $(ab)^m = a^m b^m$.
(6) $\left(\dfrac{a}{b}\right)^m = a^m/b^m$.

(Cases (2) and (4) should be carefully distinguished.)

If the indices, m and n, are not positive integers, but are fractional, zero, or negative, the methods of proof, based on the fundamental laws of algebra, fail; it is meaningless to speak of multiplying a quantity by itself $3\frac{1}{2}$ times, or -4 times, or 0 times. To find a meaning for such expressions as $a^{\frac{1}{2}}$, or a^{-2}, or a^0, we *assume* that the fundamental Index Law

$$a^m \times a^n = a^{m+n},$$

is true for *all* values of m and n, including fractional, negative, and zero values; and then proceed to find what interpretation must be put on a^m for these values. We at the same time tacitly assume that an algebraic law which

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is proved under certain restrictions is true generally provided that the removal of these restrictions is not *incompatible* with the truth of the law.

Interpretation of fractional indices.

Consider $a^{\frac{m}{n}}$, where m and n are positive integers.

$$\left(a^{\frac{m}{n}}\right)^n = a^{\frac{m}{n}} \times a^{\frac{m}{n}} \times \ldots \text{to } n \text{ factors}$$
$$= a^{\frac{m}{n} + \frac{m}{n} + \ldots \text{ to } n \text{ terms}}$$
$$= a^{\frac{m}{n} \times n} = a^m,$$
$$\therefore a^{\frac{m}{n}} = \sqrt[n]{\left(a^{\frac{m}{n}}\right)^n} = \sqrt[n]{a^m}.$$

Thus $a^{\frac{m}{n}}$ is the nth root of a^m.

Thus $a^{\frac{1}{2}} = \sqrt[2]{a},\ a^{\frac{1}{3}} = \sqrt[3]{a},\ a^{\frac{2}{5}} = \sqrt[5]{a^2}.$

Interpretation of the zero index.

$a^m \times a^n = a^{m+n}$ for *all* values of m and n.

Put $m = 0$ $\therefore$ $a^0 \times a^n = a^{0+n} = a^n$

$$\therefore a^0 = \frac{a^n}{a^n} = 1.$$

Thus any *finite* quantity raised to zero power equals unity. (Notice that we have not yet found a meaning for 0^0, which is indeterminate.)

Interpretation of a negative index.

In the equation $a^m \times a^n = a^{m+n}$, put $m = -n$,
$$\therefore a^{-n} \times a^n = a^{-n+n} = a^0 = 1.$$
Thence $a^{-n} = 1/a^n.$

a^{-n} is therefore the reciprocal of a^n.

Thus $a^{-2} = 1/a^2,\ a^{-\frac{1}{2}} = 1/a^{\frac{1}{2}} = 1/\sqrt{a}.$

Results in indices :—

$$a^m \times a^n = a^{m+n}$$
$$a^m/a^n = a^{m-n}$$
$$a^{-m} = 1/a^n$$
$$a^{\frac{1}{n}} = \sqrt[n]{a}$$
$$a^{\frac{m}{n}} = \sqrt[n]{a^m}$$
$$a^0 = 1.$$

29. EXPONENTIAL FUNCTIONS

Any function which contains the *independent variable* in the *index* is called an *Exponential Function*.

Examples :—

$$a^x, (a + x)^{-x}, a^{x^2}.$$

Before proceeding to the differentiation of such functions, we will give a brief account of the properties of logarithms. The student is assumed to be acquainted with the elementary treatment.

30. LOGARITHMS

$$\text{Let } a^x = y,$$

where a is any fixed quantity.

From the results of indices we saw that

$$a^0 = 1$$

if a is finite. We now consider the value of a^x when x becomes *infinite*.

(i) Let $|a| > 1$, where $|a|$ denotes the *numerical* value of a.

Then $|a^2| > |a|$, $|a^3| > |a^2|$, and so. Thus if x increases without limit, a^x increases without limit,

$$\text{or } a^x \to +\infty \text{ as } x \to +\infty.$$
$$\text{Again } a^{-x} = 1/a^x = 1/\infty = 0$$
$$\text{or } a^{-\infty} \to 0.$$

(ii) Let $|a| < 1$. Put $a = 1/b$, then if $|a| > 1$, $|b|$ will be < 1, which is the case we wish to investigate.

$$b^x = 1/a^x = 1/\infty = 0 \text{ when } x \to \infty,$$
$$\therefore b^\infty \to 0 \text{ if } |b| < 1.$$
$$\text{Again } b^{-x} = 1/b^x = 1/0 = \infty \text{ if } x \to \infty.$$

Let us now suppose that a in

$$a^x = y$$

is a fixed positive quantity, greater than unity. Then if x ranges from $-\infty$ to $+\infty$, y will range from 0 to $+\infty$.

If we imagine the series of indices (x), and powers (y) tabulated for a given value of a, then the indices will constitute a table of *logarithms* of the corresponding numbers in the table of powers, a being called the *base*.

Thus if $a^x = y$,
$$x = \log_a y \quad \textit{(Definition of logarithm)}.$$

The *logarithm* of a number to a given *base* is the *index* of that power of the base which is equal to the given number.

Thus $\log_4 256 = 4$, because $4^4 = 256$.

From the above discussion it follows that
$$\log_a(+\infty) = \infty,$$
$$\log_a 0 = -\infty,$$
where a is any base greater than unity.

The equations $\log_a(a^n) = n$,
$$a^{\log_a x} = x,$$
are seen to be identities in the light of the definition.

We shall now prove some important properties of logarithms, these being true for any base:—

(1) Since $a^\circ = 1$ $\therefore \log_a 1 = 0$.

(2) Since $a^1 = a$ $\therefore \log_a a = 1$.

(3) $\log_a MN = \log_a M + \log_a N$.

For let $\log_a M = m$,
$$\log_a N = n,$$
then $M = a^m$,
$$N = a^n, \text{ by definition.}$$
Thence $MN = a^m \times a^n = a^{m+n}$
$$\therefore \log_a MN = \log_a a^{m+n} = m + n,$$
$$= \log_a M + \log_a N.$$

(4) $\log_a \dfrac{M}{N} = \log_a M - \log_a N$,

by a similar proof.

(5) $\log_a M^n = n \log_a M$,

where n is positive or negative, integral or fractional.

For let $\log_a M = m$,
$$\therefore a^m = M.$$
Then $M^n = (a^m)^n = a^{mn}$,
$$\therefore \log_a M^n = \log_a a^{mn} = mn = n \log_a M.$$

Corollary. $\log_a \sqrt[n]{M} = \dfrac{1}{n}\log_a M$.

31. LOGARITHMS TO DIFFERENT BASES

Let a, b be two different fixed numbers adopted as the bases of two systems of logarithms, and let M be any positive number.

$$\text{Let } \log_a M = x, \log_b M = y.$$
$$\text{Then } M = a^x, \text{ and } M = b^y,$$
$$\therefore a^x = b^y$$
$$\therefore a = \left(a^x\right)^{\frac{1}{x}} = b^{\frac{y}{x}},$$
$$\text{and } b = a^{\frac{x}{y}}.$$
$$\text{Thus } \frac{y}{x} = \log_b a, \frac{x}{y} = \log_a b,$$
$$\therefore y = x \log_b a = \frac{x}{\log_a b},$$
$$\therefore \log_b M = \log_a M \cdot \log_b a = \frac{\log_a M}{\log_a b}.$$

Thus, to transform any logarithm to a given base to another base, we divide it by the logarithm of the second base with respect to the first base.

$\dfrac{1}{\log_a b}$ is often called the *modulus* of the second system with respect to the first.

32. RESULTS IN INDICES AND LOGARITHMS

$a^x = y$	$x = \log_a y$
$a^0 = 1$	$\log_a 1 = 0$
$a^1 = a$	$\log_a a = 1$
$a^{\frac{1}{n}} = \sqrt[n]{a}$	$\log_a \sqrt[n]{a} = \dfrac{1}{n}$
$a^{-1} = 1/a$	$\log_a(1/a) = -1$
$a^{\infty} = \infty \, (a > 1)$	$\log_a \infty = \infty$
$a^{-\infty} = 0 \, (a > 1)$	$\log_a 0 = -\infty$
$a^x a^y = a^{x+y}$	$\log_a xy = \log_a x + \log_a y$
$a^x/a^y = a^{x-y}$	$\log_a \dfrac{x}{y} = \log_a x - \log_a y.$
$(a^x)^n = a^{nx}$	$\log_a x^n = n \log_a x$
$\sqrt[n]{a^x} = a^{x/n}$	$\log_a \sqrt[n]{x} = \dfrac{1}{n}\log_a x.$

33. SYSTEMS OF LOGARITHMS.

With regard to the value of the base adopted, it may be said that two systems of logarithms are in common use, each being characterized by particular advantages.

(1) The *Common Logarithms*, or *Briggsian Logarithms* (introduced by Henry Briggs of Oxford, b. 1556, d. 1630) are to the base 10.

$$\text{Thus } \log_{10}2 = 0\cdot3010300. . .,$$
$$\text{because } 10^{0\cdot3010300} . . . = 2.$$

These have the advantage that the base is at the same time the radix of the common scale of notation. Numbers having the same figures, but differing in the position of the decimal point, will therefore have common logarithms differing by a positive or negative integer only. This leads to a very considerable abridgment of the logarithm tables.

Proof. Let M, N be numbers differing only in the position of the decimal point, e.g. 106·4, and 1·064. Then

$$M = N \times \text{some integral power of } 10 = N \times 10^n,$$
$$\therefore \log_{10}M = \log_{10}N.10^n = \log_{10}N + n\log_{10}10$$
$$= \log_{10}N + n.$$

(2) The *Natural, Hyperbolic*, or *Napierian Logarithms* (John Napier, b. 1550, d. 1617) are calculated to a base called e, where e is an incommensurable quantity. To seven places

$$e = 2\cdot7182818. . . .$$

These are related to a number of important theorems in higher mathematics, which will be considered in the sequel. Natural logarithms are denoted by "$\log_e$," or "ln," or, in mathematical works, simply by "log," the base e being understood.

Since the equation

$$\log_a y = x, \text{ if } y = a^x,$$

is true for *all* bases,

$$\log_e y = x, \text{ if } y = e^x;$$

or if a is a constant,

$$\log_e y = ax, \text{ if } y = e^{ax}.$$

This is the definition of $\log_e$.

To convert natural logarithms into common logarithms, they must be multiplied by the modulus of the common logarithms, i.e. by $\log_{10}e$, usually denoted by μ. Thus

$$\log_{10}M = \mu \cdot \log_e M = \log_e M \cdot \log_{10}e = \frac{\log_e M}{\log_e 10}.$$

34. HISTORICAL NOTE

John Napier in 1614 published a table of natural sines and their logarithms, but these were not to the base e, although closely related to such logarithms. Henry Briggs took up Napier's idea, and developed it with great enthusiasm, publishing in 1617 his "Logarithmorum chilias prima," containing common logarithms of numbers from 1 to 1000. Logarithms to the base e, often incorrectly called "Napierian logarithms," were first tabulated by John Speidell ("New Logarithmes," London, 1619).

35. THE COMPOUND INTEREST LAW

Let a capital of c pounds be invested at compound interest of p per cent per annum.

Interest after the lapse of one year $= c\dfrac{p}{100}$,

$\therefore$ capital at the beginning of the second year

$$= c_1 = c + c\frac{p}{100} = c\Big(1 + \frac{p}{100}\Big).$$

Capital at the end of the second year

$$= c_2 = c_1 + c_1\frac{p}{100} = c\Big(1 + \frac{p}{100}\Big)^2.$$

The capital at the end of n years is thus

$$c_n = c\Big(1 + \frac{p}{100}\Big)^n.$$

Thus, as the *time* increases in *arithmetical progression*, the *capital* increases in *geometrical progression*.

Now suppose the interest, instead of being added yearly, is added monthly. At the end of the first month the capital is

$$c_1 = c + c \cdot \frac{p}{100 \times 12} = c\Big(1 + \frac{p}{100 \times 12}\Big);$$

at the end of the second month it is

$$c_2 = c_1\left(1 + \frac{p}{100 \times 12}\right) = c\left(1 + \frac{p}{100 \times 12}\right)^2;$$

and after n months it is

$$c_n = c\left(1 + \frac{p}{100 \times n}\right)^n;$$

e.g. after a year, $n = 12$, and

$$c_{12} = C = c\left(1 + \frac{p}{100 \times 12}\right)^{12}.$$

Putting $p = 5$ we find, by using logarithms, that the capital after 1 year is

£105 0s. 0d. if reckoned by the first method;

£105 2s. 0d. if reckoned by the second;

the principal being £100 in each case.

(A very interesting account of compound interest and its calculation in various cases is given by Briggs and Bryan, "Tutorial Algebra," ch. xviii.) Now if the interest be added weekly, daily, or every second, we approach more and more closely to an ideal limiting case in which the interest on a given capital *at any instant* is proportional to the capital at that instant. The capital is then *increasing at a rate proportional to itself.* Processes of this kind are common in nature. If in unorganized or organized nature, a process proceeds in such a way that an agent, by its own mode of operation, steadily augments, the increment originating at every instant at once acquiring the functions of the operating agent, then the increase follows the Compound Interest Law. The mathematical expression for a function y, which increases with respect to another variable x at a rate proportional to itself is

$$dy/dx = y.$$

Lord Kelvin has called this "the Compound Interest Law in Nature".

To derive this from the case just considered, we put, instead of $\dfrac{p}{12 \times 100}$, the term $\dfrac{p}{100n}$, where n is ultimately

greater than any magnitude, however large, and denote $p/100$ by x. Then

$$C = c \operatorname*{Lim}_{n \to \infty} \left(1 + \frac{x}{n}\right)^n.$$

Let $x/n = 1/\delta$ $\therefore$ $n = \delta.x$,

$$\left(1 + \frac{x}{n}\right)^n = \left(1 + \frac{1}{\delta}\right)^{\delta x} = \left[\left(1 + \frac{1}{\delta}\right)^\delta\right]^x.$$

It is required to find the limiting value of $\left(1 + \frac{1}{\delta}\right)^\delta$ when $\delta \to \infty$.

By the Binomial Theorem

$$\left(1 + \frac{1}{\delta}\right)^\delta = 1 + \frac{\delta}{\delta} + \frac{\delta.\delta - 1}{2!}\frac{1}{\delta^2} + \frac{\delta.\delta - 1.\delta - 2}{3!}\frac{1}{\delta^3} + \ldots$$

$$= 1 + \frac{1}{1} + \frac{1 - \frac{1}{\delta}}{2!} + \frac{\left(1 - \frac{1}{\delta}\right)\left(1 - \frac{2}{\delta}\right)}{3!} + \ldots$$

The limiting value of this expression, when δ approaches infinity, is the sum of the infinite series

$$1 + \frac{1}{1} + \frac{1}{2!} + \frac{1}{3!} + \ldots \text{ to infinity.}$$

We denote this sum by the letter e. The value of e can be calculated to any desired degree of approximation by taking a sufficiently large number of terms of the series. To five places

$$e = 2\cdot71828\ldots.$$

$$\text{Now } C = c \operatorname*{Lim}_{n \to \infty} \left(1 + \frac{x}{n}\right)^n,$$

$$\text{and } \operatorname*{Lim}_{n \to \infty} \left(1 + \frac{x}{n}\right)^n = e^x,$$

$$\therefore \underline{C = ce^x},$$

which is a second way of writing the compound interest law.

The series

$$e^x = 1 + \frac{x}{1} + \frac{x^2}{1 \cdot 2} + \frac{x^3}{1 \cdot 2 \cdot 3} + \frac{x^4}{1 \cdot 2 \cdot 3 \cdot 4} + \ldots \text{ ad inf.,}$$

$$= 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \ldots \text{ ad inf.,}$$

is called the *Exponential Series*; it is true *for all values of x*.

36. IMPORTANT SERIES

Two other important series are given below, the proofs being deferred until Taylor's Theorem has been considered :—

(1) $a^x = 1 + \frac{x}{1}\log_e a + \frac{x^2}{1 \cdot 2}(\log_e a)^2 + \frac{x^3}{1 \cdot 2 \cdot 3}(\log_e a)^3 + \ldots$ ad inf.,

for all values of x.

This may be regarded as a generalized form of the exponential series.

(2) $\log_e(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \frac{x^5}{5} - \ldots$ ad inf.,

for $|x| < 1$.

An expansion of $\log_e x$ alone in a series of ascending powers of x cannot be derived, but it is easy to show by putting $x = -x$ in (2) that :

(2a) $\log_e(1 - x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \ldots$ ad inf.

37. CALCULATION OF NATURAL LOGARITHMS

Series (2) and (2a) may be modified in different ways, and the resulting series are often more convenient than the original series.

Thus $\log_e \frac{1+x}{1-x} = \log_e(1 + x) - \log_e(1 - x)$

$$= 2\left\{x + \frac{x^3}{3} + \frac{x^5}{5} + \frac{x^7}{7} + \ldots\right\}.$$

Now let $1 + x = m$, $1 - x = n$,

$$\therefore x = \frac{m - n}{m + n},$$

$$\frac{1 + x}{1 - x} = \frac{m}{n},$$

$$\therefore \log_e \frac{m}{n} = 2\left\{\frac{m - n}{m + n} + \frac{1}{3}\left(\frac{m - n}{m + n}\right)^3 + \frac{1}{5}\left(\frac{m - n}{m + n}\right)^5 + \ldots\right\}.$$

Put $n + 1 = m$,

$$\therefore \log_e \frac{n + 1}{n} = 2\left\{\frac{1}{2n + 1} + \frac{1}{3(2n + 1)^3} + \frac{1}{5(2n + 1)^5} + \ldots\right\};$$

which enables one to find the logarithm of the second of two successive integers when the logarithm of the first is known. A table of natural logarithms may thus be formed, commencing with $\log_e 2$:—

$$\log_e \frac{n + 1}{n} = 2\left\{\frac{1}{2n + 1} + \frac{1}{3(2n + 1)^3} + \ldots \text{etc.}\right\}.$$

Put $n = 1$,

$$\therefore \log_e 2 = 2\left\{\frac{1}{3} + \frac{1}{3 \cdot 3^3} + \frac{1}{5 \cdot 3^5} + \frac{1}{7 \cdot 3^7} + \ldots\right\}.$$

The method of calculation is exhibited below :—

				$1/3 =$	$\cdot 333,333,333$
$1/3^3 = (1/3)$	$\div 9 =$	$\cdot 037,037,037$	$\therefore 1/(3 \cdot 3^3)$	$=$	$12,345,679$
$1/3^5 = (1/3^3)$	$\div 9 =$	$4,115,226$	$\therefore 1/(5 \cdot 3^5)$	$=$	$823,045$
$1/3^7 = (1/3^5)$	$\div 9 =$	$457,247$	$\therefore 1/(7 \cdot 3^7)$	$=$	$65,321$
$1/3^9 = (1/3^7)$	$\div 9 =$	$50,805$	$\therefore 1/(9 \cdot 3^9)$	$=$	$5,645$
$1/3^{11} = (1/3^9)$	$\div 9 =$	$5,645$	$\therefore 1/(11 \cdot 3^{11})$	$=$	513
$1/3^{13} = (1/3^{11})$	$\div 9 =$	627	$\therefore 1/(13 \cdot 3^{13})$	$=$	48
$1/3^{15} = (1/3^{13})$	$\div 9 =$	70	$\therefore 1/(15 \cdot 3^{15})$	$=$	5
$1/3^{17} = (1/3^{15})$	$\div 9 =$	8	$\therefore 1/(17 \cdot 3^{17})$	$=$	0

$$\cdot 346,573,589$$
$$2$$

$$\cdot 693,147,178$$

$$\therefore \log_e 2 = \cdot 693147180 \text{ to 9 places.}$$

We now put $n = 2$ in the series for $\log_e \dfrac{n + 1}{n} = \log_e 3$ $- \log_e 2$; and since $\log_e 2$ is known, the value of $\log_e 3$ is found by adding to $\log_e 2$ the value of the right-hand member of the series. Similarly $\log_e 4$, $\log_e 5$, . . . are found.

E.g. $\log_e 5 - \log_e 4 = 2\left\{\dfrac{1}{9} + \dfrac{1}{3 \cdot 9^3} + \dfrac{1}{5 \cdot 9^5} + \ldots\right\}.$

It is only necessary, however, to calculate the prime numbers, for

$$\log_e 4 = \log_e 2 + \log_e 2 = 2 \times \cdot 693147180,$$
$$\log_e 10 = \log_e 5 + \log_e 2, \text{ etc.}$$

88. CALCULATION OF COMMON LOGARITHMS

To calculate the common logarithms, we should theoretically have to multiply each member of the table of natural logarithms by μ, the modulus of the common logarithms. In practice, a much less laborious direct method is used.

In the equation

$$\log_e \frac{n+1}{n} = 2\left\{\frac{1}{2n+1} + \frac{1}{3(2n+1)^3} + \frac{1}{5(2n+1)^5} + \ldots\right\}$$

we observe that the error committed by neglecting all terms beyond the first will be less than

$$2\left\{\frac{1}{3(2n+1)^2} + \frac{1}{3(2n+1)^3} + \frac{1}{3(2n+1)^4} + \ldots\right\}$$
$$< 2 \cdot \frac{1}{3(2n+1)^2}\bigg/\left(1 - \frac{1}{2n+1}\right)$$
$$< 2\frac{1}{3(2n+1)^2} \cdot \frac{2n+1}{2n} = \frac{1}{3n(2n+1)}.$$

If n is not less than 10,000, this error will be less than $\frac{1}{3 \cdot 10000 \cdot 20001}$, i.e. $< \cdot 000000001$, and will not affect the eighth place of decimals in the logarithm. Thus, if we retain only the first term :—

$$\log_e \frac{n+1}{n} = \frac{2}{2n+1}$$
$$\therefore \log_{10} \frac{n+1}{n} = \frac{2\mu}{2n+1}$$
$$\therefore \log_{10}(n+1) = \log_{10}n + \frac{2\mu}{2n+1}.$$

This will serve to calculate common logarithms to seven places, because we can commence with

$$\log_{10}10000 = 4,$$

and logarithms of numbers less than 10000 will differ only from those above 10000, with the same significant

6

digits, by the values of their characteristics, i.e. the figures before the decimal place.

$$\text{Thus } \log_{10} 536 \cdot 4 = \log_{10} 53640 - 2.$$

We have treated the exponential and logarithmic functions at some length, because they play a most important part in the practical applications of mathematics. A very large number of natural processes are of the type contemplated by the compound interest law, and exponential terms occur constantly in the equations of physics and chemistry. If, in any process, a function is found to be increasing or decreasing at a rate proportional to itself, it may be inferred to be an exponential function.

39. THE GRAPH OF THE EXPONENTIAL FUNCTION

$$\text{Let } y = e^x.$$

If, corresponding to each value of x as abscissa, we erect an ordinate proportional to e^x, and join the ends of the ordinates, we obtain the graph of the exponential function. Tables giving the values of e^x are to be found in most collections of mathematical tables, and may be used in drawing the graph. A short table of values will be found in appendix (6). A good idea of the shape of the curve may, however, be obtained without actually plotting the values of e^x, but simply by noticing the character of the function $y = e^x$:—

(1) As x increases from 0 to $+ \infty$, y increases from $+ 1$ to $+ \infty$. The curve will therefore cut the y axis at $y = 1$, and will then recede more and more from the x axis.

(2) As x decreases from 0 to $- \infty$, y decreases from 1 to 0, but much more gradually than in (1), since the curve starts from the ordinate $y = + 1$.

(3) For all positive and negative values of x, the value of y is positive. The curve will therefore lie wholly above the x axis. Thus $e^{-x} = 1/e^x$, and is therefore positive.

The graph of e^x is seen on inspection to have all these characteristics.
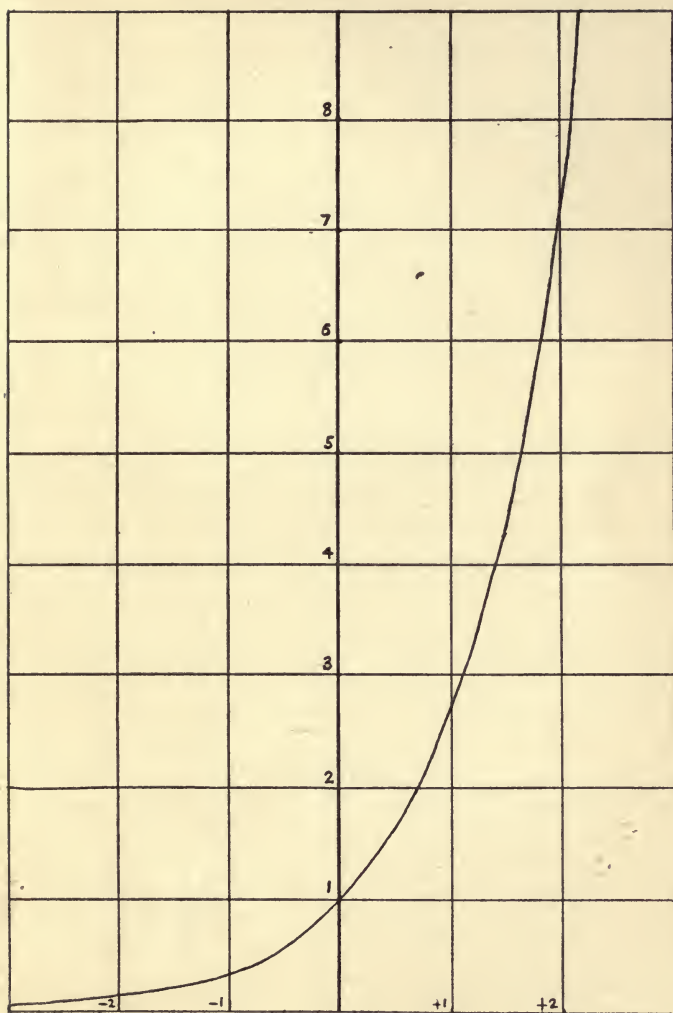
Fig. 13.

(The graph of $y = e^{-x}$ may be derived from the data for $y = e^x$, since $e^{-x} = 1/e^x$. The ordinate for any value of the abscissa is therefore the reciprocal of the ordinate in the graph of e^x for the same value of the abscissa.) The shape and position of the curve must be remembered.

40. EXAMPLES ON EXPONENTIAL AND LOGARITHMIC FUNCTIONS

(1) Prove from the definition of logarithm that :—
  (a) if $y = e^{\log_e x}$, then $y = x$;
  (b) if $\log_e y_o - \log_e y = kct$, then $y = y_o e^{-kct}$;
  (c) if $\log_e U = \dfrac{\phi}{c} - \dfrac{R}{c}\log_e v$, then
  $$U = e^{\frac{\phi}{c}} . v^{\frac{R}{c}}.$$

(2) Show that if x is positive
$$\log_e x = \frac{x-1}{x+1} + \frac{1}{2}.\frac{x^2-1}{(x+1)^2} + \frac{1}{3}.\frac{x^3-1}{(x+1)^3} + \dots$$
$$\left[Hint.\ x = \left(1 - \frac{1}{x+1}\right) \Big/ \left(1 - \frac{x}{x+1}\right). \right]$$

(3) Prove that if $x > 2$,
$$\log_e(x^2 + 3x + 2) = 2\log_e x + \left(\frac{2+1}{x} - \frac{2^2+1}{x^2} + \frac{2^3+1}{x^3}\dots\right).$$

(4) Show that
$$\text{Lim} \sqrt[x]{\frac{1+x}{1-x}} = e^2.$$
$$x \to 0$$

(5) Show that
$$\log_e 2 - \frac{1}{2} = \frac{1}{1.2.3} + \frac{1}{3.4.5} + \frac{1}{4.5.6} + \dots$$
$$[2\log_e 2 = 2(1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \dots) = \text{etc.}]$$

(6) Show that
$$\text{Lim} \frac{e^x - e^{-x}}{\log(1+x)} = 2.$$
$$x \to 0$$

[If we substitute $x = 0$ directly in the expression, we obtain

$$\frac{e^0 - 1/e^0}{\log(1 + 0)} = \frac{1 - 1}{\log 1} = \frac{0}{0},$$

which is known as a *vanishing fraction*. The value of $\frac{0}{0}$ being indeterminate, it is necessary to ascertain if the expression has any finite limit when x approaches zero. This is easily done by expansion into series.]

(7) If x is so small that its square and higher powers are negligible, show that

$$e^{e^x} = e(1 + x).$$

(8) If $a(\log y + x) = l \log x + m$,
   show that $x^l = y^a \cdot e^{ax - m}$.

[In transforming logarithmic functions into exponentials or vice versa, the student is recommended to write down the fundamental equation :—

$$y = a^x \text{ if } x = \log_a y,$$

and compare the symbols with those in the example, after collecting logarithmic terms.]

(9) Expand $e^x(1 - x)$ in a series of ascending powers of x. $\left[1 - \dfrac{x^2}{2} - \dfrac{x^3}{3 \cdot 1!} - \dfrac{x^4}{4 \cdot 2!} - \dfrac{x^5}{5 \cdot 3!} - \cdots \right]$

(10) Prove that

$$2 \log_e m - \log_e(m + 1) - \log_e(m - 1)$$
$$= 2\left\{ \frac{1}{2m^2 - 1} + \frac{1}{3(2m^2 - 1)^3} + \frac{1}{5(2m^2 - 1)^5} + \cdots \right\}$$

(11) Prove that

$$\log_e\left(\frac{1}{1 - x}\right) = x + \frac{x^2}{2} + \frac{x^3}{3} + \cdots.$$

(12) Expand $\log_e(x^2 + 5x + 6)$ in a series of descending powers of x.

$$\left[2 \log_e x + \left\{ \frac{3 + 2}{x} - \frac{1}{2} \cdot \frac{3^2 + 2^2}{x^2} + \frac{1}{3} \cdot \frac{3^3 + 2^3}{x^3} - \cdots \right\} \right]$$

41. DIFFERENTIATION OF THE EXPONENTIAL FUNCTION

We shall first prove that the exponential series

$$1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$$

is convergent for all values of x.

The first term is 1, the second is $\frac{x}{1}$, the third is $\frac{x^2}{2!}$, and, generally, the nth term is $\frac{x^{n-1}}{(n-1)!}$. Thus if u_{n+1}, u_n are the $(n+1)$th and nth terms

$$\frac{u_{n+1}}{u_n} = \frac{x}{n}.$$

$$\therefore \underset{n \to \infty}{\text{Lim}} \frac{u_{n+1}}{u_n} = 0, \text{ since } \underset{n \to \infty}{\text{Lim}} \frac{x}{n} = 0$$

for all values of x.

Then, by method 2 of testing the convergency of a series (see " Infinite Series "), we conclude that the exponential series is convergent.

It must not be supposed, however, that the series obtained by *differentiating* a convergent series term by term is also convergent. Thus the series

$$1 + x^1 + x^{1 \cdot 2} + x^{1 \cdot 2 \cdot 3} + x^{1 \cdot 2 \cdot 3 \cdot 4} + \ldots$$

is convergent for $|x| < 1$, but the series

$$1 + 2x + 6x^5 + \ldots,$$

obtained by differentiation, is divergent for all values of x.

It can be shown, however, that the series obtained by differentiating the exponential series term by term is uniformly convergent, hence the differentiation is legitimate.

$$\text{Let } y = e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$$

$$\therefore dy = d(e^x) = \left(1 + x + \frac{x^2}{2!} - \ldots\right)dx$$

$$= e^x dx.$$

$$\text{Hence } \frac{d(e^x)}{dx} = e^x,$$

and thus e^x satisfies the condition for a function $y = f(x)$

such that the differential coefficient is equal to the function itself; or the rate of increase of the function is equal to the value of the function :

$$dy/dx = y.$$

Corollary 1.—The graph of $y = e^x$ cuts the y axis at an angle of $45°$.

Corollary 2.—At any point on the graph of $y = e^x$, the gradient is equal to the value of the ordinate.

42. TESTS FOR AN EXPONENTIAL FUNCTION

There are two methods of determining whether one variable is increasing (or decreasing) exponentially with another, which are frequently used in practice.

$$(1) \text{ Let } y = ae^{bx}$$

be an exponential function ; a and b being constants. If any two values of y are taken, one being double the other, and if x_1, x_2 are corresponding values of x :

$$y_1 = ae^{bx_1},$$
$$y_2 = ae^{bx_2}.$$
$$\text{But } y_1 = \tfrac{1}{2}y_2,$$
$$\therefore \tfrac{1}{2}y_2 = ae^{bx_1} \qquad . \qquad . \qquad . \qquad (i)$$
$$y_2 = ae^{bx_2} \qquad . \qquad . \qquad . \qquad (ii)$$

Dividing (i) by (ii) we get

$$\tfrac{1}{2} = e^{b(x_2 - x_1)},$$

or $x_2 - x_1 = (\log_e \tfrac{1}{2})/b = a$ *constant.*

Thus if x increases in arithmetical progression, y increases (or decreases) in geometrical progression. The curve of the function is drawn, and the increase in value of x for an increase of y to double, or a decrease to half, its value, is found on different parts of the curve.

These increments of x are *all equal* if the curve is exponential. The student may easily test this rule on the curve of e^x, fig. 13.

$$(2) \text{ Let } y = ae^{bx}, \text{ as before.}$$
$$\text{Then } \log_e y = \log_e a + bx.$$

This is of the form

$$y' = a' + bx,$$

where $y' = (\log_e y)$, $a' = (\log_e a) = $ constant.
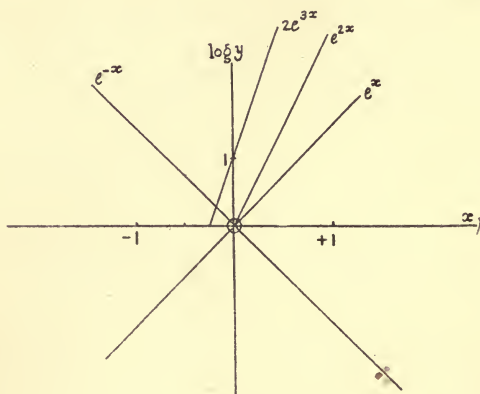
F<small>IG</small>. 14.

But this is the equation of a straight line. If therefore $(\log_e y)$ is plotted against x, the result will be a straight line if y is an exponential function of x. The length intercepted on the y (i.e. $\log_e y$) axis is $\log_e a$, and the slope of the line is b.

If $a = 0$, $\log_e a = 0$, and the line passes through the origin.

The lines for $y = e^x$, $y = e^{-x}$, $y = e^{2x}$, $y = 2e^{3x}$, are drawn in the figure.

Thus, in the case of $y = 2e^{3x}$,

$$(\log_e y) = \log_e 2 + 3x$$
$$= \cdot 693 + 3x.$$

The intercept is ·693, and the gradient $+ 3$.

This method is of frequent application in chemical kinetics, as will be illustrated later on.

43. DIFFERENTIATION OF LOG x

Let $y = \log_e x$,

$\therefore x = e^y$, by definition of logarithm.

$$dx = d(e^y) = d(e^{\log_e x}),$$
$$\therefore dx = e^{\log_e x} \cdot d(\log_e x),$$
$$\therefore dx = x \cdot d(\log_e x),$$
$$\therefore d(\log_e x) = \frac{dx}{x}, \text{ or } \frac{d(\log_e x)}{dx} = \frac{1}{x}.$$

This result is of the utmost importance.

44. EXAMPLES

(1) If $y = e^{ax}$, $dy = ae^{ax}$.

(2) If $y = \log_a x$, $dy = \dfrac{dx}{x \log_e a}$.

If $a = 10$, $dy = dx/x \log_e 10$

$$= \frac{\mu dx}{x} = 0.4343 \frac{dx}{x}.$$

(3) If $y = \log u$, where $u = f(x)$,

$$dy = \frac{du}{u}, \frac{dy}{dx} = \frac{1}{u} \cdot \frac{du}{dx}.$$

(4) Let $y = \dfrac{1}{2} \log \dfrac{1+x}{1-x}$,

then $dy = \frac{1}{2}\dfrac{dx}{1+x} - \frac{1}{2}\dfrac{dx}{1-x} = \dfrac{dx}{1-x^2}$.

(5) If $y = \log\{x + \sqrt{x^2 \pm 1}\}$

$$dy = \frac{dx}{\sqrt{x^2 \pm 1}}.$$

This result is often very useful in effecting an integration (see Part II).

(6) If $y = \log\dfrac{x}{\sqrt{x^2 + 1}}$, $dy = \dfrac{dx}{x(x^2 + 1)}$.

(7) If $y = \log\dfrac{x}{\sqrt{(x^2 + 1)} - x}$, $dy = \dfrac{dx}{x} + \dfrac{dx}{\sqrt{x^2 + 1}}$.

(8) If $y = \log\dfrac{1 + x + x^2}{1 - x + x^2}$, $dy = \dfrac{2(1 - x^2)}{1 + x^2 + x^4}$.
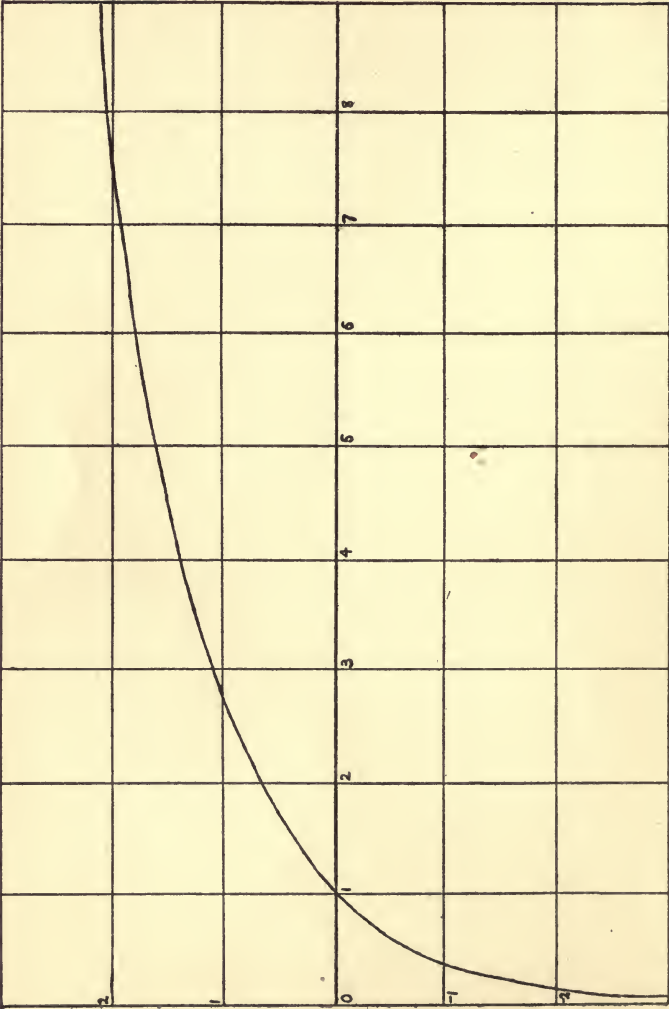
Fig. 15.

45. GRAPH OF THE LOGARITHMIC FUNCTION

Let $y = \log_e x$.

Plotting values of y corresponding to given *positive* values of x by means of the tables, one obtains fig. 15.

$$\log_e e = 1 \qquad \log_e e^2 = 2 \qquad \log_e e^3 = 3, \ldots$$
$$\log_e \frac{1}{e} = -1 \qquad \log_e \frac{1}{e^2} = -2 \qquad \log_e \frac{1}{e^3} = -3. \ldots$$

$\therefore x =$	0	$\frac{1}{e^2}$	$\frac{1}{e}$	1	e	$e^2 + \infty$
$y =$	$-\infty$	-2	-1	0	1	$2 + \infty$
$dy/dx =$	$+\infty$	e^2	e	1	$\frac{1}{e}$	$\frac{1}{e^2}$ 　0

From the properties of e^x and $\log_e x$ it is evident that if the axes of x and y are interchanged, in fig. 15, we have the graph of the exponential function. $\text{Log}_e x$ and e^x are said to be *inverse functions*.

The following characteristics should be noted :—

(1) As x increases from $+1$ to $+\infty$, y increases slowly from 0 to $+\infty$.

(2) As x decreases from $+1$ to 0, y decreases rapidly from 0 to $-\infty$.

(3) The function does not exist for negative values of x.

(4) The tangent to the curve makes an angle with the x-axis decreasing from 90° at $x = 0$, through 45° at $x = 1$, to 0° at $x = +\infty$

$$(dy/dx = \tan a = 1/x \therefore \text{ when}$$
$$x = 0 \qquad\qquad 1 \qquad +\infty$$
$$1/x = \tan a = \infty \qquad 1 \qquad 0$$
$$\therefore a = 90° \qquad\qquad 45° \qquad 0°).$$

The shape and position of the curve should be remembered.

46. THE DIFFERENTIATION OF a^x

$$\text{Let } y = a^x$$
$$\therefore y = e^{x\log_e a}.$$
$$(\because \log_e y = \log_e a^x = x \log_e a$$
$$\therefore y = e^{x\log_e a}.)$$
$$\text{Thence } dy = d(e^{x\log_e a}) = \log_e a \,.\, e^{x\log_e a} dx$$
$$\therefore \underline{d(a^x) = \log_e a \,.\, a \,.\, dx.}$$

47. LOGARITHMIC DIFFERENTIATION

Logarithmic differentiation is a method of differentiating complicated functions involving exponentials or powers. It consists simply in taking logarithms before differentiating.

$$\text{Let } y = u \,.\, v \,.\, w,$$
where u, v, w are given functions of x.
$$\text{Then } \log y = \log u + \log v + \log w$$
$$\therefore d(\log y) = d(\log u) + d(\log v) + d(\log w)$$
$$\therefore \frac{dy}{y} = \frac{du}{u} + \frac{dv}{v} + \frac{dw}{w}$$
$$\therefore dy = vw \,.\, du + uw \,.\, dv + uv \,.\, dw.$$

48. EXAMPLES

(1) If $y = x^x$, show that
$$dy = x^x(1 + \log x)dx.$$

(2) If $y = (ax + b)^a \,.\, (cx + d)^\beta / (ex + f)^\gamma$, show that
$$dy/y = \left[\frac{a a}{ax + b} + \frac{c\beta}{cx + d} - \frac{e\gamma}{ex + f}\right]dx.$$

(3) $y = \sqrt{\dfrac{a + 2bx + cx^2}{a - 2bx + cx^2}}.$
$$\left[\frac{dy}{dx} = \frac{2b(a - cx^2)}{(a - 2bx + cx^2)^{\frac{3}{2}}(a + 2bx + cx^2)^{\frac{1}{2}}}.\right]$$

(4) $\qquad y = u^v,$
where u, v are functions of x.
$$\log y = v \log u$$
$$\frac{dy}{y} = v\frac{du}{u} + \log u \,.\, dv$$
$$\therefore dy = v \,.\, u^{v-1} \,.\, du + u^v \,.\, \log u \,.\, dv.$$

If $u = a^x$, $v = x$
$$y = a^{a^x},$$
and $dy = xa^{a^{x-1}}dx + a^{a^x}\log a^x dx.$

(5) $y = \log x^n$. $\left[dy = \dfrac{nx^{n-1}dx}{x^n} = n\dfrac{dx}{x}. \right]$

(6) $y = \log(\log x)$. $\left[dy = \dfrac{d(\log x)}{\log x} = \dfrac{dx}{x \log x}. \right]$

(7) $y = x^2 \log x$. $[dy = \{2 \log x + 1\}x dx.]$

(8) $y = x^n,$
$\therefore \log y = n \log x,$
$$dy = nx^{n-1}dx.$$

(9) $y = e^x \left\{ \dfrac{x+1}{x-1} \right\}^{\frac{1}{2}}$

$\log y = x + \frac{1}{2}\log(x+1) - \frac{1}{2}\log(x-1).$

$$dy = y(dx - dx/(x^2-1) = e^x \cdot \dfrac{(x^2-2)}{(x+1)^{\frac{1}{2}}(x-1)^{\frac{3}{2}}}dx.$$

(10) The *order* of a chemical reaction is defined as the value of n in the velocity equation (Ostwald). Thus
$$dx/dt = k(a-x)^n.$$
Put $a - x = c$, the concentration,
$$dc = -dx$$
$$\therefore dc/dt = -kc^n.$$

Let the initial concentrations be different in two cases, say c_1, c_2. Then
$$dc_1/dt = -kc_1^n$$
$$dc_2/dt = -kc_2^n$$
$$\therefore \frac{dc_1/dt}{dc_2/dt} = c_1^n/c_2^n$$
$$\therefore \log\frac{dc_1}{dt} - \log\frac{dc_2}{dt} = n(\log c_1 - \log c_2)$$
$$\therefore n = \frac{\log\dfrac{dc_1}{dt} - \log\dfrac{dc_2}{dt}}{\log c_1 - \log c_2}.$$

The values of $\dfrac{dc_1}{dt}$, $\dfrac{dc_2}{dt}$ can be found experimentally by measurements at the beginning of the reaction.

(11) Magnus's empirical formula for the vapour pressure of water at $\theta°$ C. is

$$p = ab^{\frac{\theta}{r+\theta}},$$

where a, b, r are constants.

Show that $dp/d\theta = \dfrac{ar \log b}{(r+\theta)^2} \cdot b^{\frac{\theta}{r+\theta}}$.

(12) The intensity of radioactivity of radium emanation decays with the time according to an exponential law

$$\mathrm{I} = \mathrm{I}_0 e^{-\lambda t},$$

where I_0, I = activities at times 0, t,
λ = the radioactive constant.

Thence $\dfrac{d\mathrm{I}}{dt} = -\lambda \mathrm{I}$.

This shows that the rate of decay at any instant is proportional to the activity at that instant.

This is an example of the *Compound Interest Law* :

If $y = Ce^{ax}$,
$dy/dx = aCe^{ax} = be^{ax}$,

where C, a, and $b = a$C, are constants.

Show that C is the value of y when $x = 0$.

According as a is $+^{\,ve}$ or $-^{\,ve}$ y increases or decreases as x increases. The function Ce^{ax} therefore satisfies the equation

$$df(x)/dx = kf(x),$$

where k is a constant. Other examples of such functions are given below.

(13) Newton's Law of Cooling.

If a body at a temperature θ is placed in an enclosure at a temperature θ_0, where $\theta > \theta_0$, the body cools by radiation until the temperatures of the body and enclosure are equal. Newton assumed that, when $\theta - \theta_0$ is small, the rate of cooling is proportional to the difference of temperature :

$$d\theta/dt = -k(\theta - \theta_0).$$

Thence show that

$$\theta = be^{-at},$$

where a and b are constants.

$$a = \frac{1}{t_2 - t_1}\log_e\frac{\theta_1}{\theta_2}.$$

Newton's law holds only when $\theta_1 - \theta_0$ is small, as in most calorimeter experiments. Stefan and Boltzmann have shown theoretically and experimentally that the rate of emission of energy from a " perfectly black body " is proportional to the fourth power of its absolute temperature ;

$$dE/dt = -kT^4$$

(Haber, " Thermodynamics of Gas Reactions "; Waidner and Burgess, " Optical Pyrometry," Washington).

(14) *Absorption of Light.*—The rate of diminution in the intensity of a beam of homogeneous light passing through an absorbing medium is proportional at every point in the medium to the intensity of the light at that point. Let $x = $ thickness of medium traversed,

$$dI/dx = -aI,$$

where $a = $ extinction coefficient.

If $I_0 = $ initial intensity $(x = 0)$,

$$I = I_0 e^{-ax}.$$

(15) Show that the time t which is required for a radio-active preparation to decay to half its intensity is a definite and characteristic constant (" time period ") for each radio-active substance. We have

$$I = \tfrac{1}{2}I_0$$
$$\text{and } I = I_0 e^{-\lambda t}$$
$$\therefore \tfrac{1}{2} = e^{-\lambda t}$$
$$\therefore \log_e\tfrac{1}{2} = -\lambda t$$
$$\therefore t = \frac{\log_e 2}{\lambda} = \text{constant} = k.$$

For different substances

$$t_1 = \log_e 2/\lambda_1 = k_1,$$
$$t_2 = \log_e 2/\lambda_2 = k_2, \text{ etc.}$$

(16) *The Course of a Chemical Reaction.*—According to the law of mass-action, the rate at which a substance is disappearing in a chemical reaction is proportional to its

concentration at any instant. This is at once suggestive of the compound interest law. If c is the concentration at any instant, the mathematical expression of the mass-law is

$$dC/dt = -kC,$$
$$\text{hence } C = C_0 e^{-kt},$$

where C_0 = concentration at time $t = 0$, i.e. at the beginning of the reaction.

The amount of active substance therefore disappears exponentially with the time. To obtain a graphic representation we put $C_0 = 1$ and plot the C,t curves for different values of k. This has been done in fig. 16 for $k = 1, 2, 5, 10$. It will be observed that when k is large the curve approaches the t-axis more rapidly than when k is small; this obviously corresponds with a more rapid reaction. It is also evident that, although the curve approaches the t-axis more and more closely as t increases, it never coincides with it in finite time, but only when $t = +\infty$. This means that a chemical reaction is, theoretically, never finished. The amount of unchanged substance left after a finite time, even after a very short time, may, however, be far too small to allow of its being detected.

Thus the reaction $c = e^{-10t}$ is practically finished after
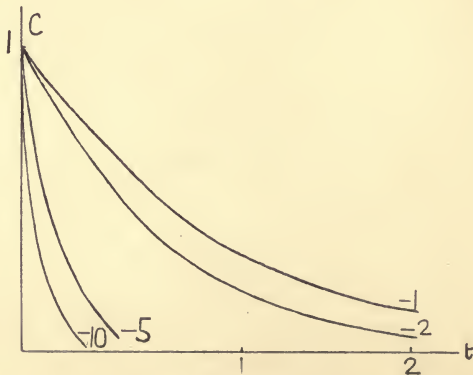
FIG. 16.

0·5 mts. ; whilst the reaction $c = e^{-t}$ is not complete after 2 mts.

The constant k, called the *velocity constant*, may be evaluated by the logarithmic method :—

$$c = e^{-kt}, \text{ for } c_0 = 1,$$
$$\therefore \log_e c = -kt.$$

If therefore $\log_e c$ is plotted against t, a straight line is obtained, running down from the origin below the t-axis,
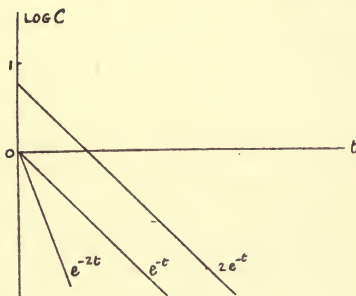
Fig. 17.

and having a gradient $= -k$. If c_0 is the initial concentration (where $c_0 \neq 1$), the curve starts on the log c axis at a point $\log_e c_0$, and slopes downwards as before. If a few measurements are made near the beginning of the reaction, the initial concentration c_0 may be found by plotting the straight line, as described, and prolonging it backwards to cut the $\log_e c$ axis. The point where it cuts this axis corresponds to $\log_e c_0$, whence c_0 is easily found.

7

CHAPTER VI

PARTIAL DIFFERENTIATION

49. PARTIAL DIFFERENTIAL COEFFICIENTS

UP to the present we have been considering functions of *one* independent variable. The majority of magnitudes investigated in physics and chemistry are, however, functions of two or of several independent variables. Examples of such functions are :—

(1) The volume of a gas, which depends on the temperature (θ) and the pressure (p),

$$v = f(p, \theta).$$

If the gas obeys Boyle's and Charles's laws

$$v = \frac{R\theta}{p}.$$

(2) The area (A) of an ellipse is a function of its semi-axes a and b,

$$A = f(a, b).$$

(3) The volume (V) of a rectangular prism is a function of the lengths of its edges

$$V = f(x, y, z).$$

In conformity with previous notation, we shall speak of v, say, in example (1), as the *dependent variable ;* p and θ as the *independent variables*.

Now functions of several independent variables are of special interest in chemistry, because the properties of a given material system depend not only on the temperature and pressure, but also on the chemical composition. If there are n components in the mass, there will be $n + 1$ independent variables, including temperature and pressure.

50. PARTIAL DIFFERENTIALS

Let us consider, for simplicity, the area of a rectangle, as determined by the lengths of its sides.

$$A = xy \qquad . \qquad . \qquad . \qquad (1)$$

Let the edges x, y be increased by very small amounts dx, dy, and let dA_x, dA_y be the increments of area due to each of the increments dx, dy considered as independent. From the figure
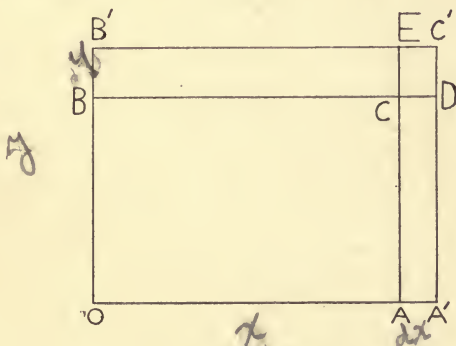
Fig. 18.

$$dA_x = y\,dx \qquad . \qquad . \qquad . \qquad (2)$$
$$dA_y = x\,dy \qquad . \qquad . \qquad . \qquad (3)$$
$$\therefore \frac{dA_x}{dx} = y, \; \frac{dA_y}{dy} = x.$$

We denote these differential coefficients by

$$\frac{\partial A}{\partial x}, \; \frac{\partial A}{\partial y} \qquad . \qquad . \qquad . \qquad (4)$$

where $\partial A/\partial x$ is to be understood as "the rate of increase of A with x when y is constant". In the example

$$\frac{\partial A}{\partial x} = y, \; \frac{\partial A}{\partial y} = x \qquad . \qquad . \qquad . \qquad (5)$$

$\partial A/\partial x$ and $\partial A/\partial y$ are called the *Partial Differential Coefficients* with respect to x and y respectively. Thus

$$dA_x = \frac{\partial A}{\partial x}dx\,; \; dA_y = \frac{\partial A}{\partial y}dy \qquad . \qquad . \qquad (6)$$

But $\delta A = AA'CD + BB'CE + CDEC'$
$$= dA_x + dA_y + dx\,dy \qquad . \qquad . \qquad . \qquad (7)$$

In the limit, when dx and dy approach the value zero,

$$dA = dA_x + dA_y \qquad \qquad (8)$$

The geometrical meaning of this is quite obvious. dA is called the *Total Differential*, dA_x, dA_y the *Partial Differentials* of A. From the equations (6) and (8)

$$dA = \frac{\partial A}{\partial x}dx + \frac{\partial A}{\partial y}dy \qquad \qquad (9)$$

This equation is another example of the Principle of Superposition of small effects.

Generally, let

$$u = f(x, y) \qquad \qquad (10)$$

$$\frac{\partial u}{\partial x} = \frac{\partial}{\partial x}f(x, y) = f'(x) \text{ say . } (y \text{ const.}) \qquad (11)$$

$$du_x = \frac{\partial u}{\partial x}dx = \frac{\partial}{\partial x}f(x, y) . dx = f'(x)dx \qquad (12)$$

Similarly,

$$\frac{\partial u}{\partial y} = \frac{\partial}{\partial y}f(x, y) = f'(y) \text{ say . } (x \text{ const.}) \qquad (13)$$

$$du_y = \frac{\partial u}{\partial y}dy = \frac{\partial}{\partial y}f(x, y) . dy = f'(y)dy \qquad (14)$$

Also $du = du_x + du_y$

$$\therefore du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy$$

$$\therefore du = \frac{\partial}{\partial x}f(x, y) . dx + \frac{\partial}{\partial y}f(x, y) . dy$$

$$\therefore du = f'(x)dx + f'(y)dy.$$

51. EXAMPLES

(1) $u = ax^2 + by^2$

$$\delta u = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy + a(dx)^2 + b(dy)^2$$

$$du = 2axdx + 2bydy.$$

(2) $u = x^2 - y^2.$

$$du = 2xdx - 2ydy.$$

(3) $u = \log(x^2 + y^2).$

$$du = \frac{2(xdx + ydy)}{x^2 + y^2}$$

(4) If $pv = R\theta$, the gas law,
$$\frac{\partial p}{\partial v} = -\frac{R\theta}{v^2}; \quad \frac{\partial p}{\partial \theta} = \frac{R}{v}.$$

Interpret each differential coefficient.

52. THREE INDEPENDENT VARIABLES

In the case of a function of three independent variables,
$$u = f(x, y, z) \qquad . \qquad . \qquad . \qquad (1)$$

$$\left.\begin{aligned}
\frac{\partial u}{\partial x} &= \frac{\partial}{\partial x} f(x, y, z) = f'(x) \\
\frac{\partial u}{\partial y} &= \frac{\partial}{\partial y} f(x, y, z) = f'(y) \\
\frac{\partial u}{\partial z} &= \frac{\partial}{\partial z} f(x, y, z) = f'(z)
\end{aligned}\right\} \qquad . \qquad . \qquad (2)$$

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy + \frac{\partial u}{\partial z} dz \qquad . \qquad . \qquad . \qquad (3)$$

$$\therefore du = \frac{\partial}{\partial x} f(x, y, z) \cdot dx + \frac{\partial}{\partial y} f(x, y, z) \cdot dy + \frac{\partial}{\partial z} f(x, y, z) dz$$

$$\therefore du = f'(x) dx + f'(y) dy + f'(z) dz.$$

Example :—

Let u be the volume of a rectangular prism
$$u = xyz.$$
$$du = yz\,dx + xz\,dy + xy\,dz.$$

This gives the increase in volume due to slight increments in the lengths of the sides.

53. FUNCTIONS OF FUNCTIONS

$$\text{Let } u = F(x, y) \qquad . \qquad . \qquad . \qquad (1)$$
$$\text{where } x = f(t), \ y = \phi(t) \qquad . \qquad . \qquad (2)$$

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy$$

$$\therefore \frac{du}{dt} = \frac{\partial u}{\partial x} \cdot \frac{dx}{dt} + \frac{\partial u}{\partial y} \cdot \frac{dy}{dt} \qquad . \qquad . \qquad (3)$$

$$\therefore \frac{du}{dt} = \frac{\partial u}{\partial x} f'(t) + \frac{\partial u}{\partial y} \phi'(t) \qquad . \qquad . \qquad (4)$$

$$\text{If } u = F(x, y, z). \qquad . \qquad . \qquad (5)$$
$$\text{where } x = f(t), \ y = \phi(t), \ z = \psi(t) \qquad . \qquad (6)$$

$$\frac{du}{dt} = \frac{\partial u}{\partial x} f'(t) + \frac{\partial u}{\partial y} \phi'(t) + \frac{\partial u}{\partial z} \psi'(t) \ . \qquad (7)$$

As examples consider the coefficients of superficial and cubical expansion. Both these are ultimately functions of temperature (θ).

$$\text{Let } \sigma = \frac{ds}{d\theta},$$

where s is unit surface. σ is, by definition, the coefficient of superficial expansion. Considering a plate of a non-isotropic material cut with its edges x, y, parallel to the two axes of expansion, the surface is

$$S = xy \qquad \qquad (1)$$

$$dS = \frac{\partial S}{\partial x}dx + \frac{\partial S}{\partial y}dy \qquad (2)$$

But $\partial S/\partial x = y$, $\partial S/\partial y = x$ . . (3)

$$\therefore \frac{dS}{d\theta} = y\frac{dx}{d\theta} + x\frac{dy}{d\theta} \qquad (4)$$

Let $x = y = 1$,
$$\therefore dS/d\theta = ds/d\theta = \sigma,$$
$$\text{and } \sigma = \frac{dx}{d\theta} + \frac{dy}{d\theta},$$

or the sum of the coefficients of linear expansion is equal to the coefficient of superficial expansion.

To obtain a numerical relation, we may assume with sufficient accuracy that x and y are linear functions of θ:—

$$x = 1 + \lambda_1\theta,$$
$$y = 1 + \lambda_2\theta,$$
$$\therefore \sigma = \lambda_1 + \lambda_2 \qquad (5)$$

In the case of cubical expansion,

$$V = xyz . \qquad \qquad (6)$$

$$\frac{dV}{d\theta} = yz\frac{dx}{d\theta} + xz\frac{dy}{d\theta} + xy\frac{dz}{d\theta} \qquad (7)$$

If $x = y = z = 1$,
$$dV/d\theta = a, \text{ the coefficient of cubical expansion,}$$

$$\therefore a = \frac{dx}{d\theta} + \frac{dy}{d\theta} + \frac{dz}{d\theta} . \qquad (8)$$

the sum of the coefficients of linear expansion along the three axes. With the same assumption as before

$$x = 1 + \lambda_1\theta,$$
$$y = 1 + \lambda_2\theta,$$
$$z = 1 + \lambda_3\theta,$$
$$\therefore a = \lambda_1 + \lambda_2 + \lambda_3 \quad . \quad . \quad . \quad (9)$$

Formulæ (5) and (9) must be used for crystalline bodies, the properties of which depend on the direction in the crystal along which the property is measured. In the case of an isotropic body, such as a piece of glass, the properties of which are uniform in all directions in the mass,

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda, \text{ say,}$$
$$\therefore \sigma = 2\lambda,$$
$$a = 3\lambda, \quad . \quad . \quad . \quad (10)$$

the well-known equations of elementary physics.

54. SIDE REACTIONS

If several chemical reactions are proceeding simultaneously in a given system, each progresses independently of the others, and the total change is the sum of the separate changes. (Principle of the Mutual Independence of Reactions.)

Considering two unimolecular reactions progressing simultaneously, a principal reaction and a side reaction
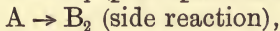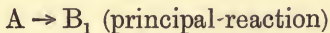
$$A \rightarrow B_1 \text{ (principal-reaction)}$$
$$A \rightarrow B_2 \text{ (side reaction),}$$
$$dx_1/dt = k_1(a - x) \text{ for the first reaction,}$$
$$dx_2/dt = k_2(a - x) \text{ for the second reaction;}$$

also, total velocity = sum of separate velocities,

$$\therefore dx/dt = dx_1/dt + dx_2/dt$$
$$= (k_1 + k_2)(a - x).$$

In the nitration of benzoic acid in presence of excess of nitrating acid, the three isomeric mononitrobenzoic acids are produced simultaneously at different rates.

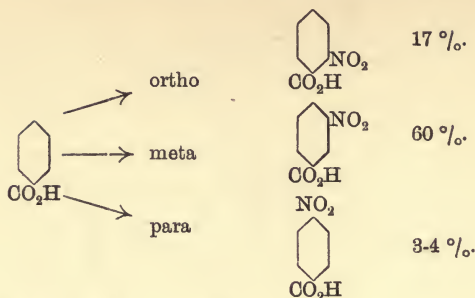The velocity of the reaction is

$$dx/dt = (k_1 + k_2 + k_3)(a - x).$$

55. THERMODYNAMICS

Partial differential coefficients appear very frequently in textbooks on thermodynamics, and since the whole of modern theoretical chemistry is based upon the fundamental laws of thermodynamics, it is of the utmost importance that the chemical student should be able to realize at once the significance of such a partial differential coefficient in any mathematical deduction from those laws. We assume that the student has an elementary knowledge of the First and Second laws, and their applications.

According to the system of J. Willard Gibbs ("On the Equilibrium of Heterogeneous Substances," "Collected Works," Vol. I, Longmans), which is of particular interest to chemists, the state of a homogeneous gaseous, liquid, or solid phase is (in the absence of electric and magnetic forces, and when the energy due to gravity or to capillarity (surface-tension) can be neglected completely defined by some law connecting the variables p, v, θ; the pressure, volume, and absolute temperature, respectively. Thus

$$f(p, v, \theta) = 0 \qquad . \qquad . \qquad . \qquad (1)$$

(Thus a mass of liquid water satisfies the condition mentioned above; a very small drop of water does not, because the surface-energy is not negligibly small in comparison with the total internal energy of the drop. As a

matter of fact, the vapour-pressure of water in the form of small drops is greater than that over a horizontal surface of water at the same temperature, and the pressure is then not completely defined by the temperature and volume of a given mass. If the drop is electrified, its vapour-pressure is diminished, but the same statement holds good.)

Any one variable·is therefore completely defined if the values of the remaining two are fixed thus

$$p = f_1(v, \theta) \qquad . \qquad . \qquad . \qquad (2)$$
$$v = f_2(p, \theta) \qquad . \qquad . \qquad . \qquad (3)$$
$$\theta = f_3(p, v) \qquad . \qquad . \qquad . \qquad (4)$$

In the case of a perfect gas

$$pv - R\theta = 0$$
$$\therefore \; p = \frac{R\theta}{v}, \; v = \frac{R\theta}{p}, \; \theta = \frac{pv}{R}.$$

A very large number of equations may now be obtained by the partial differentiation of equations (2) to (4). A few examples are given below. Let

$$p = f_1(v, \theta)$$
$$dp = \frac{\partial p}{\partial v}dv + \frac{\partial p}{\partial \theta}d\theta \quad . \qquad . \qquad . \qquad (5)$$

Obviously

$\partial p/\partial v$ = coefficient of increase of pressure with volume at constant temperature

= coefficient of elasticity.

For all real states, $\partial p/\partial v$ is negative, otherwise the pressure would increase along with the volume.

$\partial p/\partial \theta$ = coefficient of increase of pressure with increase of temperature at constant volume.

If we make the condition that the pressure is constant, i.e. the change is *isopiestic*,

$$dp = 0 \quad . \qquad . \qquad . \qquad . \qquad (6)$$
$$\therefore \; \left(\frac{dp}{dv}\right)_\theta dv = - \left(\frac{dp}{d\theta}\right)_v d\theta$$
$$\text{or} \; \left(\frac{dv}{d\theta}\right)_p = - \left(\frac{dp}{d\theta}\right)_v \bigg/ \left(\frac{dp}{dv}\right)_\theta \quad . \qquad (7)$$

(where $\left(\dfrac{dp}{dv}\right)_\theta$ is another way of writing "$\dfrac{\partial p}{\partial v}$ at constant temperature". The ordinary notation $\partial p/\partial v$ loses definiteness when there are more than two variables.) $dv/d\theta$ must be written $(dv/d\theta)_p$ by reason of condition (6).

Equation (7) states that the ratio of the increase of pressure at constant volume per 1° rise in temperature, to the compressibility is equal to the coefficient of expansion at constant pressure.

Proceeding in the same way with equations (3) and (4), one finds the relations

$$\left(\frac{dp}{d\theta}\right)_v = -\left(\frac{dv}{d\theta}\right)_p \bigg/ \left(\frac{dv}{dp}\right)_\theta,$$
$$\left(\frac{dv}{dp}\right)_\theta = -\left(\frac{d\theta}{dp}\right)_v \bigg/ \left(\frac{d\theta}{dv}\right)_p.$$

In the case of mercury,

$$(dv/d\theta)_p = 0.00018 \text{ c.c. per } 1° \text{ C.,}$$
$$(dv/dp)_\theta = -0.000003 \text{ c.c. per 1 atm.,}$$
$$\therefore (dp/d\theta)_v = 60 \text{ atm. per } 1° \text{ C.}$$

This means that an increase of pressure of 60 atm. is required to keep the volume of 1 c.c. of mercury constant when it is warmed from 0° C. to 1° C. (Planck, "Thermodynamik".)

Further examples on Thermodynamics will be found in Part II. (Integral Calculus.)

56. HIGHER PARTIAL DERIVATIVES

It has been stated that if

$$y = f(x),$$

$dy/dx = f'(x)$ is called the *first derivative* of y. This will usually be a function of x.

E.g. if $y = x^3$,
$$f'(x) = 3x^2.$$

The first derivative may thus be differentiated with respect to x, and the result is denoted by $\dfrac{d^2y}{dx^2} = f''(x)$, and

called the *second derivative*.   In the example taken, $f''(x) = 6x$.

In general, the nth derivative is denoted by $\dfrac{d^n y}{dx^n}$, or $f^n(x)$.

Examples :—

(1) Find the values of $f''(x)$, or $\dfrac{d^2 y}{dx^2}$, if

$$y = x^2(1 - x)^2. \quad [2 - 12x + 12x^2.]$$
$$y = \tfrac{1}{48}\mu x^2(3l^2 - 4lx + 2x^2). \quad [\tfrac{1}{2}\mu(x - \tfrac{1}{2}l)^2.]$$

(2) Find the value of $\dfrac{d^3 y}{dx^3}$ if

$$y = x^2 e^x. \quad [(x^2 + 6x + 6)e^x.]$$

In the same way we may have higher *partial* derivatives.   If

$$u = \phi(x, y),$$

then *four* second derivatives are *a priori* possible, viz.

$$\frac{\partial^2 u}{\partial x^2}, \frac{\partial^2 u}{\partial x \partial y}, \frac{\partial^2 u}{\partial y \partial x}, \frac{\partial^2 u}{\partial y^2}.$$

It can be shown, however, that under certain conditions which are usually satisfied in practice, the second and third are identical; that is, the result is *independent of the order of differentiation*,

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x} \qquad . \qquad . \qquad . \qquad (1)$$

This result is exceedingly important.

Examples :—

(1) Let $\quad u = xy$

$$\frac{\partial u}{\partial x} = y, \frac{\partial u}{\partial y} = x;$$
$$\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial}{\partial y} \cdot \frac{\partial u}{\partial x} = 1; \ \frac{\partial^2 u}{\partial x \partial y} = 1.$$

(2) Let $\quad u = x^2 + y^2.$

$$\frac{\partial u}{\partial x} = 2x, \ \frac{\partial u}{\partial y} = 2y$$
$$\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y} = 2.$$

(3) Let $\quad u = x^2 + y^2 + x^2y^3$

$$\frac{\partial u}{\partial x} = 2x + 2xy^3 ; \quad \frac{\partial u}{\partial y} = 2y + 3x^2y^2 ;$$

$$\frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y} = 2 + 6y^2x.$$

57. PERFECT DIFFERENTIALS

Let $f(x, y)$, $\phi(x, y)$ be two functions of the independent variables x and y, and suppose that

$$du = f(x, y)dx + \phi(x, y)dy \quad . \quad . \quad (1)$$

It by no means follows from (1) that du is a differential of a finite quantity u which is a function of x and y, considered as independent variables. In some cases it is, in others it is not; and in order that u may be a function of x and y, a certain condition must be fulfilled by the functions $f(x, y)$ and $\phi(x, y)$.

If du is the differential of a function u of x and y,

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy \quad . \quad . \quad . \quad (2)$$

Comparing (1) with (2), we see that the condition that u in (1) is a function of x and y is

$$f(x, y) = \frac{\partial u}{\partial x}, \phi(x, y) = \frac{\partial u}{\partial y} \quad . \quad . \quad (3)$$

$$\text{But } \frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y}$$

$$\therefore \frac{\partial}{\partial y}f(x, y) = \frac{\partial}{\partial x}\phi(x, y) \quad . \quad . \quad (4)$$

is the condition that du in (1) is the differential of a function u of x and y. Under these circumstances du is called a *Perfect Differential*, and equation (4) is known as *Euler's criterion* that the expression on the right of equation (1) is a perfect differential. If we write (1) in the form

$$Mdx + Ndy \quad . \quad . \quad . \quad (5)$$

where M, N are functions of x and y, the condition that (5) is a perfect differential is

$$\partial M/\partial y = \partial N/\partial x \quad . \quad . \quad . \quad (6)$$

This relation is exceedingly important, occurring repeatedly in thermodynamics, and must be remembered.

Examples. Show that the following expressions are perfect differentials :—

$$(ax + hy + g)dx + (hx + by + f)dy ;$$
$$x(x + 2y)dx + (x^2 - y^2)dy ;$$
$$(3y^2x - x^2)dy + (y^3 - 2xy)dx ;$$
$$(x^2 - 4xy - 2y^2)dx + (y^2 - 4xy - 2x^2)dy.$$

Show that the following expressions are not perfect differentials :—

$$ydx + 5xdy,$$
$$ydx - (x + y^2)dy.$$

58. MAXIMA AND MINIMA OF FUNCTIONS OF TWO VARIABLES

If $y = f(x)$, the necessary, but not sufficient, condition that y has a maximum or a minimum value is that x shall have a value which satisfies the equation

$$\frac{dy}{dx} = f'(x) = 0.$$

If $u = f(x, y)$, i.e. is a function of two variables, then it can be shown that, for a maximum or a minimum value of u, it is necessary but not sufficient that

$$\frac{\partial u}{\partial x} = 0 \text{ and } \frac{\partial u}{\partial y} = 0 \text{ simultaneously.}$$

If it can be otherwise inferred that a maximum or minimum value exists, and the discrimination between them effected, then the condition just given is sufficient.

59. EXAMPLES

(1) Find the rectangular parallelepiped of least surface for a given volume.

Let x, y, z be the edges, a^3 the volume.

Then $xyz = a^3$.

The surface $= u = 2(xy + yz + zx)$.

We have to find the relations existing between x, y, and z so that u shall be a minimum. Now u can be

expressed as a function of two variables, x and y, since $z = \dfrac{a^3}{xy}$, and a^3 is, by hypothesis, constant.

Thus $u = xy + \dfrac{a^3}{x} + \dfrac{a^3}{y}$.

$$\frac{\partial u}{\partial x} = y - \frac{a^3}{x^2}, \quad \frac{\partial u}{\partial y} = x - \frac{a^3}{y^2}.$$

The condition for a maximum or minimum value of u requires that x and y shall have values which satisfy the simultaneous equations

$$y - \frac{a^3}{x^2} = 0 . \qquad . \qquad . \qquad . \qquad \text{(i)}$$

$$x - \frac{a^3}{y^2} = 0 \qquad . \qquad . \qquad . \qquad \text{(ii)}$$

Thus $x^2 y = xy^2$

$\therefore x(xy) = y(xy),$

and unless $xy = 0$, which cannot be the case,

$x = y = a$, and $\therefore z = a$, or

$x = y = z$.

The equation $u = xy + \dfrac{a^3}{x} + \dfrac{a^3}{y}$

shows that the surface must have a minimum value, since x and y are positive. Thus the required figure is a cube.

(2) Find the condition which must subsist between the initial concentrations a and b so that the velocity of reaction shall be a maximum in a bimolecular reaction.

$$dx/dt = V = k(a - x)(b - x)$$

$$\therefore \frac{\partial V}{\partial a} = - k(b - x) ; \quad \frac{\partial V}{\partial b} = - k(a - x).$$

The conditions $\partial V/\partial a = 0$, $\partial V/\partial b = 0$, lead to

$$a = b.$$

It is easy to see that this corresponds to a maximum value; since, by the mass-law, the velocity is increased by addition of one component or the other, and is zero for each pure component. Thus the initial concentrations must be equal.

Chapter VII

INTERPOLATION AND EXTRAPOLATION

60. INTERPOLATION

LET y be a continuous function of x

$$y = f(x) \qquad . \qquad . \qquad . \qquad (1)$$

Then corresponding to every value of x, within certain limits, there will be at least one value of y. We will further suppose y to be a single-valued function of x, then each value of x corresponds to one definite value of y.

If the form of $f(x)$ is known, then the value of y may be calculated directly for a given value of x, and the problem offers no difficulty. But if this form is not known, the process is different.

Suppose that two pairs of corresponding values of x and y, say x_1, y_1, and x_2, y_2, are known. Further, let x_1 and x_2 be nearly equal in value. It is required to find the value of y corresponding to a value of x lying between x_1 and x_2. From the conditions imposed it is evident that $(x_1 y_1)$, $(x_2 y_2)$ are two points on a curve, and it is further evident that if x_1 and x_2 are close together, the portion of the curve lying between them may be taken very approximately to be a straight line.

Let this part of the curve be supposed drawn on a large scale, as in the figure. Then, by a well-known geometrical proposition

$$(x_2 - x) : (x_2 - x_1) = (y_2 - y) : (y_2 - y_1),$$

$$\therefore y = y_2 - \frac{y_2 - y_1}{x_2 - x_1}(x_2 - x) \qquad . \qquad . \qquad (2)$$

giving the desired value of y.

This is the *Rule of Proportional Parts.*

It is essential that y shall lie between y_1 and y_2; the rule therefore fails at maximum and minimum points on the curve.

If the values of x for which corresponding values of y are known lie fairly widely apart, the rule fails. Other rules, called Interpolation Formulæ, may be used; but in practice it is usually simpler to read off the required value from a carefully drawn graph. This involves a knowledge of several values in the neighbourhood of the point
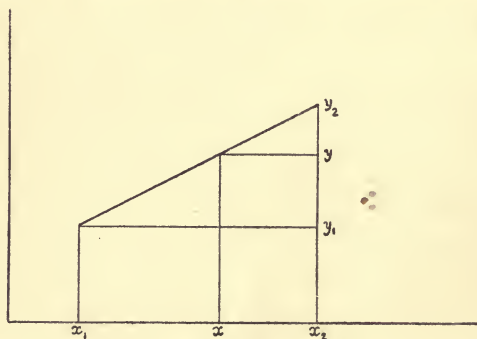
Fig. 19.

required, but so do the formulæ. It is more exact if the curve can be reduced approximately to a straight line by an appropriate change of variable (say by plotting $1/y$, or $\log y$, against x).

61. EMPIRICAL FORMULÆ

If the form of the function

$$y = f(x)$$

is not known, it is usual to endeavour to find some expression which represents, very closely at least, the relation between x and y. Thus, the vapour pressure (p) of water at a given temperature $t°$ C. was found by Biot to be given, very closely, by the equation

$$\log p = a + ba^{t-c},$$

where a, b, a, c are constants.

Such an equation is called an *Empirical Formula*, since it is not a consequence of any natural law.

In practice, one usually has accumulated a number of pairs of values of the variables, and wishes to find an equation which will represent these values. In such a case, the graph is first drawn. If the curve increases or decreases steadily, the function is probably algebraical; if it alternately increases and decreases, it is probably a trigonometrical function.

If the curve is a straight line, the equation is

$$y = a + bx,$$

where a and b are constant.

If it is not a straight line, the equation must be obtained by trial. The following forms may be applied:—

$$y = a + bx^2,$$
$$y = ax^n,$$
$$y = \frac{ax}{1 + bx},$$

$y = ae^{bx}$ (exponential function; the test for this has already been given),

$$y = \frac{a + x}{b - x},$$
$$y = 10^{a + bx},$$

($\log_{10} y$ will then give a straight line when plotted against x).

$$y = a + b \log x,$$
$$y = a + bc^x.$$

A very useful method is that depending on an application of Maclaurin's theorem (chap. IX.).

We then assume that the function may be represented by an expression of the form

$$y = a + bx + cx^2 + dx^3 + \ldots$$

The values of the constants a, b, c in any of these equations may be found by three methods:—

(1) *Algebraically*. As many pairs of values of the variables are taken as there are unknown constants, the simultaneous equations being solved by algebraic methods.

8

The equation may often be modified before this method is applied. Thus if

$$y = a \cdot 10^{\frac{bx}{1 + cx}},$$

show that

$$c = \frac{\dfrac{1}{x_2}\log\dfrac{y_2}{a} - \dfrac{1}{x_3}\log\dfrac{y_3}{a}}{\log\dfrac{y_3}{a} - \log\dfrac{y_2}{a}},$$

$$b = \frac{\log\dfrac{y_2}{a} \cdot \log\dfrac{y_3}{a}\left(\dfrac{1}{x_2} - \dfrac{1}{x_3}\right)}{\log\dfrac{y_3}{a} - \log\dfrac{y_2}{a}}$$

(a is the value of y when $x = 0$).

If we use the empirical equation,

$$y = a + bx + cx^2 + \ldots$$

it is usually sufficient to take terms up to that in x^2, and write

$$y = a + bx + cx^2 \quad . \quad . \quad . \quad (1)$$

Three points on the curve, which has been plotted from known values of x and y, are then taken, one at each end and one in the middle. Let these be (x_1, y_1), (x_2, y_2), (x_3, y_3). Substitute in (1) (which is true for every point on the curve), and we get

$$y_1 = a + bx_1 + cx_1^2$$
$$y_2 = a + bx_2 + cx_2^2$$
$$y_3 = a + bx_3 + cx_3^2.$$

These equations are now solved for a, b, c; and these values are substituted in (1). The result is

$$y = a + bx + cx^2 \quad . \quad . \quad . \quad (2)$$

in which a, b, and c are now known. a, b, c are sometimes called the *parameters* of the equation.

We now calculate, by means of (2), the values of y corresponding to those values of x for which the y values are known. A table is then drawn up containing :—

 (i) Values of x.

 (ii) Values of y from curve.

(iii) Values of y calculated from equation (2).—

(iv) Differences between observed and calculated values of y.

The differences are then plotted against the corresponding values of x, having regard to sign; and the character of the resulting curve noted. The curve may be :—

(i) A straight line parallel to the x-axis. A change in a, equal to the distance between this line and the x-axis, is required.

(ii) A straight line inclined to the x-axis, but cutting it midway between the greatest value of x and the origin. A change of b, equal to $(y_2 - y_1)/(x_2 - x_1)$ is required, where

$y_2 - y_1$ = difference between extreme ordinates,

$x_2 - x_1$ = difference between extreme abscissæ.

(iii) A straight line crossing the x-axis at some point not midway between the extreme values of x. A change in both a and b is then necessary.

(iv) A curve, concave or convex to the x-axis. A change in c, and perhaps also in a and b is then required.

In cases (iii) and (iv), it is usually easier to deduce the values of a, b, and c by another method, which takes account of all the experimental numbers. This is (2) *The Method of Least Squares.*

62. METHOD OF LEAST SQUARES

Let us suppose that the values of the constants in the equation

$$y = a + bx + cx^2 + \ldots$$

have been found by some method. Then if values of y, corresponding to values of x for which the y values are known, are calculated, these will always differ more or less from the observed values. It can be shown by the Theory of Probabilities that the most probable values of the constants a, b, c ... are those which make the sum of the squares of the differences between observed and calculated values of y as small as possible.

Let $\eta_1,\ \eta_2,\ \eta_3\ \ldots$ be the calculated,

$y_1,\ y_2,\ y_3\ \ldots$ the observed, values of y corresponding to values

$$x_1,\ x_2,\ x_3,\ \ldots\ \text{of } x.$$

The differences are $\delta_1,\ \delta_2,\ \delta_3,\ \ldots$ such that

$$y_1 + \delta_1 = \eta_1,$$
$$y_2 + \delta_2 = \eta_2,$$
$$y_3 + \delta_3 = \eta_3,$$
$$\cdots\cdots\cdots\cdots$$
$$y_n + \delta_n = \eta_n.$$

According to the theory we have just referred to, the "most probable" values of $a,\ b,\ c\ \ldots$ are those which make

$$S = \delta_1{}^2 + \delta_2{}^2 + \delta_3{}^2 + \ldots + \delta_n{}^2$$

a minimum. S will be positive if the results are affected by errors, whether positive or negative. The theoretical treatment is much too difficult to be given here, but the practical method of finding the most probable values of the constants is perfectly simple, and is in daily use. We will suppose the equation to be

$$y = a + bx + cx^2,$$

and that n pairs of values of x and y are known. $a,\ b,\ c,$ are, of course, not yet known, and we require their "most probable" values. (i) We write down in the first place, all the observation equations, substituting the values of x and y, and leaving $a,\ b,\ c$ yet undetermined. The column is then added :—

$$a + bx_1 + cx_1{}^2 - y_1 = 0$$
$$a + bx_2 + cx_2{}^2 - y_2 = 0$$
$$a + bx_3 + cx_3{}^2 - y_3 = 0$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$a + bx_n + cx_n{}^2 - y_n = 0$$
$$\therefore\ \Sigma a + \Sigma bx + \Sigma cx^2 - \Sigma y = 0,$$

where $\Sigma bx = bx_1 + bx_2 + bx_3 + \ldots + bx_n$, etc.

(ii) We then multiply each equation through by the coefficient of b (which will be a known value of x) in that equation. The column is again added.

$$ax_1 + bx_1{}^2 + cx_1{}^3 - y_1x_1 = 0$$
$$ax_2 + bx_2{}^2 + cx_2{}^3 - y_2x_2 = 0$$
$$\cdots\cdots$$
$$ax_n + bx_n{}^2 + cx_n{}^3 - y_nx_n = 0$$
$$\therefore \Sigma ax + \Sigma bx^2 + \Sigma cx^3 - \Sigma yx = 0.$$

(iii) Multiply each equation through by the coefficient of c (which will be a known value of x^2), and add the column :—

$$ax_1{}^2 + bx_1{}^3 + cx_1{}^4 - y_1x_1{}^2 = 0$$
$$ax_2{}^2 + bx_2{}^3 + cx_2{}^4 - y_2x_2{}^2 = 0$$
$$\cdots\cdots$$
$$ax_n{}^2 + bx_n{}^3 + cx_n{}^4 - y_nx_n{}^2 = 0$$
$$\therefore \Sigma ax^2 + \Sigma bx^3 + \Sigma cx^4 - \Sigma yx^2 = 0$$

By operations (i), (ii), and (iii) we arrive at what are called the three *normal equations* for a, b, c, viz.,

$$\Sigma a + \Sigma bx + \Sigma cx^2 - \Sigma y = 0.$$
$$a\Sigma x + b\Sigma x^2 + c\Sigma x^3 - \Sigma xy = 0$$
$$a\Sigma x^2 + b\Sigma x^3 + c\Sigma x^4 - \Sigma x^2 y = 0$$

These equations are linear with respect to the un-knowns, a, b, c ; being of the form

$$la + mb + nc = k,$$

where l, m, n, k, are numbers.

They are solved for a, b, c by the usual method, or preferably by determinants (see Appendix), and these are the required values of the constants.

(Further information will be found in Kohlrausch, "Leitfaden der praktischen Physik"; Mellor, "Higher Mathematics"; and especially Merriman, "Method of Least Squares".)

If the equations are linear,

$$y = a + bx,$$

the normal equations are of course

$$\Sigma a + \Sigma bx - \Sigma y = 0$$
$$a\Sigma x + b\Sigma x^2 - \Sigma xy = 0 ;$$

and so on for different forms of the general type

$$y = a + bx + cx^2 + \ldots$$

The two following examples (from Mellor, loc. cit.) will serve to illustrate the method :—

(1) Bremer gives for the expansion of solutions of sodium carbonate of percentage strength p, the following volumes :—

$$p = 3{\cdot}2420 \qquad 4{\cdot}8122 \qquad 7{\cdot}4587 \qquad 10{\cdot}1400$$
$$v \times 10^4 = 1{\cdot}766 \qquad 2{\cdot}046 \qquad 2{\cdot}343 \qquad 2{\cdot}732.$$

Assuming $v = a + bp$, show that

$$v = 0{\cdot}00012415 + 0{\cdot}00001528p.$$

(2) The temperatures at different depths in a well were found to be

$$x = 28 \qquad 66 \qquad 173 \qquad 248 \qquad 298 \qquad 400 \qquad 505 \qquad 548$$
$$\theta° = 11{\cdot}71 \quad 12{\cdot}90 \quad 16{\cdot}40 \quad 20{\cdot}00 \quad 22{\cdot}20 \quad 23{\cdot}75 \quad 26{\cdot}45 \quad 27{\cdot}70.$$

At the surface $(x = 0)$, $\theta = 10{\cdot}6$. Thence

$$\theta = 10{\cdot}6 + 0{\cdot}042096x - 0{\cdot}000020558x^2.$$

63. EXAMPLES OF INTERPOLATION AND EMPIRICAL FORMULÆ

The following examples may give the student some idea of the kinds of formulæ used in cases where a theoretical relation is not known.

(1) The dependence of specific heat on the temperature is well known. It is usual to assume it to be given by an equation of the form

$$\sigma = a + bt + ct^2.$$

Thus, Weber, in the case of diamond, found

$$t° \text{ C.} = 0 \qquad 100 \qquad 985$$
$$\sigma = 0{\cdot}095 \qquad 0{\cdot}190 \qquad 0{\cdot}459.$$

Show that

$$\sigma = 0{\cdot}095 + 0{\cdot}0096t - 0{\cdot}000001t^2.$$

Mallard and Le Chatelier give for the specific heat of CO_2 (per gram molecule)

$$\sigma = 6{\cdot}3 + 0{\cdot}00564t - 0{\cdot}00000118t^2.$$

Langen used

$$\sigma = 6{\cdot}7 + 0{\cdot}0026t.$$

(2) The dependence of the vapour-pressure of a liquid upon the temperature has been represented by a large number of empirical formulæ ;—

$$\text{de la Roche:} \quad p = ab^{\frac{\theta}{m + n\theta}},$$

$$\text{Magnus:} \quad p = ab^{\frac{\theta}{r + \theta}},$$

$$\text{Biot:} \quad ln\, p = a + ba^{\theta} - c\beta^{\theta}, \text{ etc.}$$

Horstmann used a similar formulæ to Biot's to represent the dependence of the dissociation pressure of NH_4Cl on the temperature :—

$$ln\, p = a + ba^{\tau},$$

where $\tau = t^{\circ} \text{ C.} - \text{constant.}$

(3) Bodenstein measured the degree of dissociation of HI (x) at different temperatures (t° C.) :—

$t =$	508	487·2	443	427	410	393
$x =$	0·2408	0·2340	0·2198	0·2157	0·2100	0·2058
$t =$	374	356	328	302	283	
$x =$	0·2010	0·1946	0·1885	0·1815	0·1787.	

Show that Bodenstein's results are represented by :—

$$x = 0·13762 + 0·00007221t + 0·000,000,25764t^2.$$

(4) The dependence of the intensity of radiation from a hot body on the temperature of the body was expressed by different empirical formulæ before Boltzmann showed theoretically that it was proportional to the fourth power of the absolute temperature. Thus Dulong and Petit found that their experimental results were represented by a formula :—

$$f(\theta) = Aa^{\theta} + B,$$

where $f(\theta) =$ rate of surface-loss per unit surface at absolute temperature θ; A, a, B are constants.

(5) Cauchy has expressed the relation between the refractive index (μ) of a medium, and the wave-length (λ) of light, by the equation

$$\mu = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + \dots$$

$a, b, c, \dots$ being constants.

Hartmann used the interpolation formula

$$\mu - \mu_0 = \frac{c}{(\lambda - \lambda_0)^a}.$$

(6) Van der Waals has proposed the formula

$$\log\frac{\pi}{p} = a\left(\frac{\tau}{T} - 1\right)$$

as a means of calculating the vapour pressure (p) at the absolute temperature T in terms of the critical values (π, τ). a is a constant, approximately equal to 3.

Nernst has used the equation

$$p(v_a - v_b) = RT\left(1 - \frac{p}{\pi}\right)$$

where v_a, v_b are the molecular volumes of the vapour and liquid, for the same purpose.

64. REMARKS ON INTERPOLATION FORMULÆ.

It must be observed that interpolation formulæ are simply intended to enable one to calculate, with fair accuracy at any rate, the value of some magnitude intermediate between values which have been experimentally obtained.   We cannot make any theoretical deductions from them alone.

It is possible that a purely empirical interpolation formula may be a disguised form of a theoretical law. Thus, Regnault, as a result of an extensive series of researches on the compressibility of gases, arrived at the empirical formula :—

$$\frac{p_1 v_1}{p_0 v_0} = 1 - A(m - 1) + B(m - 1)^2,$$

where $m = v_0/v_1$.

Put $v_0 = 1$, $p_0 = 1$,

$$\therefore\ pv = 1 - A\frac{1 - v}{v} + B\left(\frac{1 - v}{v}\right)^2;$$

or $pv + \dfrac{A + 2B}{v} - \dfrac{B}{v^2} = 1 + A + B.$

Now van der Waals' equation, deduced from theoretical considerations, may be written

$$pv + \frac{a}{v} - bp - \frac{ab}{v^2} = \text{R}.$$

$$\text{But } p = \frac{p_0 v_0}{v} = \frac{1}{v},$$

$$\therefore \ pv + \frac{a - b}{v} - \frac{ab}{v^2} = \text{R},$$

which is identical with Regnault's formula when

$$a - b = \text{A} + 2\text{B},$$
$$ab = \text{B},$$
$$\text{R} = 1 + \text{A} + \text{B}.$$

The converse, that a formula deduced from theoretical considerations, may agree with the results of experiment simply because it is an interpolation formula, is, of course, possible, especially if it contains several parameters.

65. EXTRAPOLATION

If the value of x, for which the corresponding y value is required, lies outside the range of values for which y is known, the value of y may sometimes be found by *extrapolation*. The curve is drawn up to the extreme value of x in the known region, and then produced without change of form as far as the value of x for which the corresponding ordinate is required. This extrapolation is most easily effected when the curve is a straight line ; in other cases a waxed black thread, or the wooden shapes used by architects, may be employed. Flexible steel bands with a lead backing are now sold, and are very convenient. It is of course assumed that the equation of the curve is the same throughout the whole region considered, and that the curve is continuous. These conditions can, in general, only be safely assumed when the range of extrapolation is small in comparison with the range of known values.

Let P_1, P, P_2 be three points having the positions relative to the known curve AB shown in the figure. Then it can be safely assumed that the point P most probably lies on the extrapolated curve. The same assumption could not be made with respect to the point Q in the set Q_1, Q,

Q_2, for the curve might equally well pass through Q_1 or Q_2, or through none of the three points.
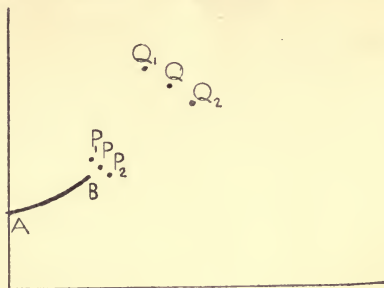

FIG. 20.

66. CAUTION.

If the curve is discontinuous, or exhibits sharp breaks or turnings, as in the solubility curve of sodium sulphate, extrapolation might lead to wholly fallacious results. Thus if the curve AP_1 had been extrapolated from x_1 to x_2,
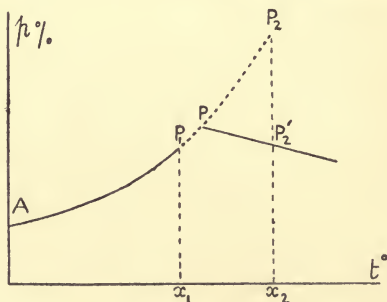

FIG. 21.

the value P_2 would be absolutely wrong; because the curve exhibits a sharp turning at P. The true value is P_2'.

The method must therefore be applied with great care.

67. EXAMPLES

(1) According to Raoult, the depression of freezing-point (A) of a solvent is proportional to the concentration.

If A is the depression for a 1 per cent solution, the molecular depression $\varDelta$ for a gram molecule in 100 c.c. will be given by

$$A : \varDelta = 1 : M,$$
$$\therefore AM = \varDelta = \text{constant},$$

since the depression is a colligative property.   This is strictly correct only for infinite dilution, so that Eykman determines the depression for three or four concentrations and then extrapolates to zero-concentration to obtain the value of A for infinite dilution.

(2) If Avogadro's law were strictly true, the molecular weight of a gas could be exactly determined by a careful
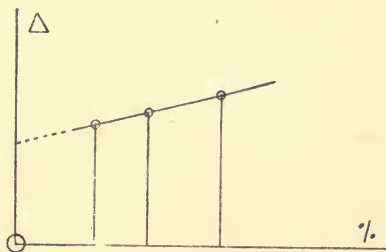
FIG. 22.

measurement of the density.   Rayleigh has found that the permanent cases obey Boyle's law more and more exactly the lower the pressure, and it may be assumed that at zero-pressure $(p = 0)$ the agreement would be exact.   D. Berthelot has made this the basis of a method of determining atomic weight from gas densities.

Van der Waals' equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

becomes, for $p = 1$ atm., and $T = 273$,

$$\left(1 + \frac{a}{v_0^2}\right)(v_0 - b) = 273\ R,$$

where $v_0 = $ molecular volume at N. T. P.

For the *ideal* gas the equation is
$$p_0 V_0 = RT \therefore V_0 = R \ . \ 273$$
where V_0 = molecular volume at N. T. P.

Thus $V_0 = v_0 \left(1 + \dfrac{a}{v_0{}^2}\right)\left(1 - \dfrac{b}{v_0}\right)$

$\therefore \ V_0 = v_0 \left(1 - \dfrac{b}{v_0} + \dfrac{a}{v_0{}^2}\right)$ approximately.

Thus, to reduce the measured density to the ideal condition it must be multiplied by
$$\frac{v_0}{V_0} = \left(1 + \frac{b}{v_0} - \frac{a}{v_0{}^2}\right) \text{ approximately.}$$

Now Van der Waals' equation may be written
$$pv = RT\left[1 + p\left(\frac{b}{RT} - \frac{a}{(RT)^2}\right)\right]$$
since a/v^2 and b/v are small compared with unity. This is of the form
$$pv = l + mp,$$
where l, and m, are constants at a fixed temperature. pv is thus a linear function of p; and if values of pv are plotted against p, the extrapolation to $p = 0$ gives the reduction to the ideal state. Such measurements have been carried out by D. Berthelot and by Guye. Recent experimenters find that in some cases pv is not really a linear function of p, but the extrapolation of the curve may still be made.

68. DIFFERENTIAL COEFFICIENTS FROM EXPERIMENTAL RESULTS

It was shown in the first part of this book that the differential coefficient has a very important significance in many branches of physical chemistry, especially in thermodynamics. In many cases, the quantity represented by this coefficient is given a special name. Thus, we recall that :—

$(dv/dt)_p$ is the coefficient of expansion at constant pressure ;

$(dp/dt)_v$, the coefficient of tension ;

$(dQ/dv)_t$, the latent heat of expansion ;

$(dQ/dt)_v$, the specific heat at constant volume ;

$(dQ/dt)_p$, the specific heat at constant pressure.

It is therefore important that we should be able to find the value of such a differential coefficient in terms of the magnitudes which are experimentally determined. We therefore pass on to a consideration of some methods of determining differential coefficients from experimental results.

69. METHOD OF MEAN-VALUE.

(I.) The first method, which may be called the *Method of the Mean-Value*, depends on the following very important theorem :—
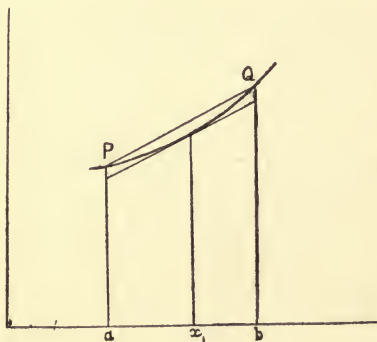
Fig. 23.

Let PQ be the graph of the function $f(x)$ which is continuous in the interval from $x = a$ to $x = b$; then there is some point between P and Q where the tangent to the curve is parallel to the secant PQ. Let x_1 be the abscissa of this point, then

$$\frac{f(b) - f(a)}{b - a} = f'(x_1).$$

This general theorem is almost obvious from an inspection of the figure; we shall assume its truth in what follows. Its connexion with the problem in hand depends on the fact that if the rate of change of $f(x)$ with x is small, as is usually the case in practical examples, we may without

committing any sensible error take x_1 midway between a and b, provided the latter are close together. Thus

$$\frac{f(b) - f(a)}{b - a} = f'\frac{(b + a)}{2} \text{ approximately.}$$

Examples :—

(1) The vapour pressures of water at $99\cdot5°$ and $100\cdot5°$ being $746\cdot52$ mm., and $773\cdot69$ mm., find dp/dt at $100°$.

$a = 99\cdot5$, $b = 100\cdot5$; $f(a) = 746\cdot52$, $f(b) = 773\cdot69$,

$$\therefore f'(100) = \frac{dp}{dt} \text{ at } 100° = 773\cdot69 - 746\cdot52$$
$$= 27\cdot17 \text{ mm. per } 1°.$$

(2) Hortsmann, in the first applications of thermodynamics to chemistry, used the well-known Clausius-Clapeyron formula :—

$$\lambda = T(v_a - v_b)\frac{dp}{dT},$$

where λ = latent heat of volatilization or dissociation,

   T = absolute temperature,

v_a, v_b = molecular volumes of gaseous and condensed phases,

   p = vapour, or dissociation, pressure.

Usually v_b is negligible compared with v_a

$$\therefore \lambda = Tv\frac{dp}{dT},$$

v being the molecular volume of the vapour.

But $pv = nRT$,

$$\therefore \lambda = \frac{nRT^2}{p} \cdot \frac{dp}{dT}.$$

If p_1, p_2 are two pressures corresponding to the temperatures T_1, T_2, which are not too far apart,

$\frac{dp}{dT} = \frac{p_2 - p_1}{T_2 - T_1}$ approximately, and in the above equation

$$p = \tfrac{1}{2}(p_1 + p_2), \ T = \tfrac{1}{2}(T_1 + T_2).$$

Horstmann considered various cases of dissociation ; as an example we will take Isambert's results for ammonium hydrosulphide :

$$NH_4HS \Longleftrightarrow NH_3 + H_2S.$$
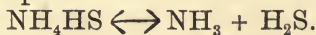
Here $n = 2$, since 2 molecules are produced. Horstmann took R = 1·997 gram-calories (the number now adopted is 1·985), so that

$$\lambda = 3·994 \frac{T^2}{p} \cdot \frac{dp}{dT} \text{ g. cal.}$$

(Observe that the unit in which p is measured does not effect the equation.)

Temperature ° C.	Pressure mm.	Heat of Dissociation Cal. at °	
9·5	175	24·65	10·7
12·0	212	21·86	13·5
15·0	259	24·24	16·5
18·0	322	20·61	20·0
22·0	410	22·64	23·5
25·1	501		

Taking the first pair of numbers we have

$$p_1 = 175 \text{ mm.}, \ p_2 = 212 \text{ mm.}$$
$$\therefore p_2 - p_1 = 37 \text{ mm.}$$
$$T_1 = 282·5°, \ T_2 = 285°,$$
$$\therefore T_2 - T_1 = 2·5.$$

Thus $dp/dT = \dfrac{p_2 - p_1}{T_2 - T_1} = \dfrac{37}{2·5} = 14·8$ mm. per 1°.

$$p = \tfrac{1}{2}(175 + 212) = 193·5 \text{ mm.}$$
$$T = \tfrac{1}{2}(282·5 + 285) = 283·7° \text{ Abs.} = 10·7° \text{ C,}$$
$$\therefore T^2 = 80486$$
$$\therefore \lambda = 3·994 \times \frac{80486}{193·5} \times 14·8 = 24650 \text{ g. cal.}$$
$$= 24·65 \text{ Cal. at } 10·7° \text{ C.}$$

(1 Cal., or " great calorie " = 1000 g. cal.)

The calculated heats of dissociation are nearly constant, the mean being 22·8 cal. This agrees with the heat of dissociation calculated from thermochemical data:

$$(NH_4HS, aq) = + 3·25 \text{ cal. (evolved)}$$
$$(NH_3 aq, H_2S aq) = + 6·19 \text{ cal.}$$
$$(H_2S, aq) = + 4·75 \text{ cal.}$$
$$(NH_3, aq) = + 8·61 \text{ cal.}$$
$$\therefore \lambda = (NH_3, H_2S) = 3·25 + 6·19 + 4·75 + 8·61 = 22·8 \text{ cal.}$$

This will, of course, be heat *absorbed* on dissociation.

(3) The Gibbs-Helmholtz equation is

$$E - q = T\frac{dE}{dT};$$

where E = electromotive force of a reversible cell,

$\quad q$ = heat absorbed when unit quantity of electricity passes round the circuit,

$\quad T$ = absolute temperature,

$\quad \dfrac{dE}{dT}$ = temperature coefficient of E.M.F.

This equation is fundamental in electrochemistry, and has been tested in a number of cases. Since E varies only slightly with temperature (about ·0001 volt per 1°), dE/dT may be found by two measurements of the E. M. F. at fairly widely separated temperatures. Thus Naumann has determined dE/dT for the gas cell

$$PtH_2/HCNaq/PtC_2N_2$$
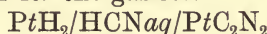
by measuring the E. M. F. at 0° C., and 50° C.

Then dE/dt at 25° C. $= \dfrac{E_{50} - E_0}{50}$ volts per 1°.

70. ALGEBRAIC METHOD.

(II.) The second method depends on the use of an empirical formula, obtained by previous calculations, to express the functional relationship. If the constants in this formula can be found, we have simply to differentiate it to obtain the desired differential coefficient.

We may call this the *Algebraic Method*.

Examples :—

(1) The pressure at constant volume (p) of isopentane is, according to Young, a linear function of the temperature ($\theta°$ C.)

$$p = b\theta - a$$
$$\therefore dp/d\theta = b,$$

or the curve is a straight line with gradient b.

(2) The vapour-pressure of water was represented by Biot according to the formula

$$lnp = a + ba^r$$

where $\tau = t° -$ constant. a, b, a are constants. By differentiation :—

$$\frac{1}{p}\frac{dp}{dt} = b \cdot lna \cdot a^\tau$$
$$\text{or } dp/dt = pblna \cdot a$$

(3) The formula used by engineers for the pressure of steam at $t°$ C. is

$$p = 29 \cdot 77 t^{1/5} - 37 \cdot 6 \text{ lb. per sq. foot.}$$

Thus $\dfrac{dp}{dt} = 5 \cdot 954 p^{-\frac{4}{5}}$.

At $t = 200°$ C.,

$$p = 29 \cdot 77 (200)^{\frac{1}{5}} - 37 \cdot 6 = 48 \cdot 44 \text{ lb./ft.}^2$$

$[\log (200)^{\frac{1}{5}} = \frac{1}{5} \log 200 = \text{etc.}]$

Thus $\left(\dfrac{dp}{dt}\right)_{t=200} = 5 \cdot 954 \times (48 \cdot 44)^{-\frac{4}{5}}$
$= 5 \cdot 954 \times \cdot 0449$
$= \cdot 267 \text{ lb. per sq. ft. per } 1° \text{ C.}$

(4) Horstmann, in his classical investigations on thermodynamics (Ostwald's *Klassiker*, No. 137, "Thermodynamik chemischer Vorgänge," August Horstmann) attempted to work out Deville's analogy between evaporation and dissociation. He concluded that Biot's formula should apply to dissociation pressures as well as to vapour pressures, and expressed the dissociation pressure of ammonium chloride by the formula

$$\log p = a + ba^\tau,$$

when $a = 5 \cdot 15790$; $b = -3 \cdot 34598$; $\log b = 0 \cdot 524394$;
$\log a = 0 \cdot 9979266 - 1$; $\tau = t°$ C. $- 258 \cdot 5$.

To calculate dp/dt at $260°$ C :—

$$\tau = 260 - 258 \cdot 5 = 1 \cdot 5 ;$$
$$\log a^{1 \cdot 5} = 1 \cdot 5 \log a = -0 \cdot 0031101,$$
$$\therefore \log a^{-1 \cdot 5} = -\log a^{1 \cdot 5} = 0 \cdot 0031101,$$
$$= \log 1 \cdot 0072,$$
$$\therefore a^{-1 \cdot 5} = 1 \cdot 0072,$$
$$\therefore a^{1 \cdot 5} = 1/a^{-1 \cdot 5} = 0 \cdot 9928.$$

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Thus $ba^{1.5} = -3.32189,$

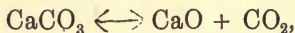$\therefore \log p = 5.15790 - 3.32189 = 1.83600.$

But $\log 68.6 = 1.83600,$

$\therefore \underline{p = 68.6 \text{ mm.}}$

Therefore $dp/dt = pba^{1.5} \log a.$

$\therefore dp/dt = 68.6 \times (-3.32189) \times (-0.00307)$

$\therefore dp/dt = 0.7039$ mm. per $1°$ C. at $260°$ C.

(5) In the case of calcium carbonate

$$\text{CaCO}_3 \Longleftrightarrow \text{CaO} + \text{CO}_2,$$

Horstmann quotes three results of Debray :—

$$
\begin{array}{ll}
t = 1040° \text{ C.} & p = 520 \text{ mm.} \\
\qquad 860 & \qquad 85 \\
\qquad 440 & \qquad \text{imperceptible.}
\end{array}
$$

He remarks that the differential coefficient dp/dt cannot be evaluated from these numbers, but he makes the assumption that the curve has the equation

$$\log p = a + ba^\tau, \qquad \qquad \text{(i)}$$

and gives the following calculation :—

Put $\tau = t - 860$, and let

$\log p$ at $860° = y_1,$

$\log p$ at $1040° = y_2.$

Then $\left.\begin{array}{l} y_1 = a + b \\ y_2 = a + ba^{180} \end{array}\right\}$ $\qquad$ (ii)

$$\therefore b = \frac{y_2 - y_1}{a^{180} - 1} \qquad \qquad \text{(iii)}$$

and $a = y_1 - b.$

Differentiating (i) with respect to t we get

$$\frac{dp}{dt} = pb \log a \,.\, a^\tau \qquad \qquad \text{(iv)}$$

$$\left.\begin{array}{l} \therefore \dfrac{dp_1}{dt} = p_1 b \log a \\[2mm] \dfrac{dp_2}{dt} = p_2 b \log a \,.\, a^{180} \end{array}\right\} \qquad \qquad \text{(v)}$$

$$\text{and } \frac{\dfrac{dp_2}{dt}}{\dfrac{dp_1}{dt}} = \frac{p_2}{p_1} \,.\, a^{180} \qquad \qquad \text{(vi)}$$

The differential coefficients (or rather, their ratio) he next expresses in terms of the heats of dissociation :—

$$\lambda = T \Delta v \frac{dp}{dT},$$

where Δv = excess of volume of gaseous product over solid residue,

= volume of gaseous product (approx.)

If s_0 = vol. of 1 kilogram CO_2 at N. T. P.,

$$\Delta v = s_0 \cdot \frac{T}{273} \cdot \frac{760}{p}, \qquad \qquad \text{(vii)}$$

where p = dissociation pressure,

$$\left. \begin{aligned} \therefore \ \lambda_1 &= s_0 \frac{760}{273} \cdot \frac{T_1^2}{p_1} \cdot \frac{dp_1}{dt} \\ \lambda_2 &= s_0 \frac{760}{273} \cdot \frac{T_2^2}{p_2} \cdot \frac{dp_2}{dt} \end{aligned} \right\} \qquad \text{(viii)}$$

$$\therefore \ \frac{\lambda_2}{\lambda_1} = \frac{T_2^2}{T_1^2} \cdot a^{180}.$$

But, λ being practically constant between 860° and 1040°, $\lambda_2/\lambda_1 = 1$,

$$\therefore \ a^{180} = \frac{T_1^2}{T_2^2},$$

and thus the constant a can be found. Then $\tau = t - 860$; $a = 3.99377$; $b = -2.06435$, log $a = 0.9988426 - 1$. From these numbers the values of p for temperatures between 860° and 1040° can be calculated.

[These calculations are now only of historical interest; modern thermodynamic theory indicates that log p can be calculated from the heat of dissociation λ, the specific heats of the substances involved, the absolute temperature, and a "chemical constant". See Nernst, "Recent Applications of Thermodynamics to Chemistry".]

71. GRAPHICAL METHOD

(III.) The third method of finding the differential coefficient of a function is the *Graphical Method*. The curve of the function is drawn on a fairly large scale, and a tangent line drawn to it at the point where dy/dx is

required. The gradient of this line, read off directly, is dy/dx.

Examples :—

(1) Horstmann used this method to calculate $dp/d\mathrm{T}$ from Debray's measurements of the vapour-pressure of Na_2HPO_4, $12H_2O$.

(2) As an exercise on the method, the student may find the values of dy/dx at different points on the graph of
$$y = x^3,$$
and compare the results with the calculated values.

(3) Using the values of p and T for water given in § 1, calculate the latent heat of evaporation of water at 100° C. The observed value is 536 cal.

[Draw the p, $(t + 273)$, curve for a few points near 100° C., draw the tangent, and find $dp/d\mathrm{T}$. Then use the Clausius-Clapeyron equation.]

Methods of finding the differential coefficient by the use of interpolation formulæ, such as Stirling's formula, can only be referred to here. (See Mellor, or Nernst-Schönflies.)

Chapter VIII

THE INDEFINITE INTEGRAL

72. INVERSE OPERATIONS AND INVERSE FUNCTIONS

WHEN, in Arithmetic, a quantity is repeated a certain number of times, the resulting quantity is called a *multiple* of the original quantity; the operation whereby it is obtained is called *multiplication*. To recover the original quantity from a given multiple of it, we make use of the operation of *division*; and the operations of multiplication and division are related in such a way that with proper values of multiplier and divisor, the effect of operating with the divisor exactly annuls the effect of previously operating with the multiplier. The symbols × and ÷ being used to denote the operations of multiplication and division respectively, and the symbol × being defined by the equation:

$$a \times n = a + a + a + \ldots n \text{ times,}$$

that of division ÷ *must* be defined by the equation:—

$$(a \times n) \div n = a.$$

The operation of division is said to be the *inverse* of the operation of multiplication, in the sense just explained.

Similarly, the processes of forming a *power* of a number, and extracting the *root* of a number are inverse operations; as is seen from the definitions of the symbols

$$a^n = a \times a \times a \times \ldots n \text{ times.}$$
$$\sqrt{a^n} = a.$$

In this particular case, the inverse operation, i.e. the extraction of the root of a quantity, is more complicated than that of division, for the following considerations enter into the nature of the case:—

(1) Whereas, in division, we arrive at the original quantity, and there is only one answer to the question: "What quantity multiplied by n leads to a given quantity?" in the extraction of the root this is not always the case.

$$na \div n = a;$$
$$\text{but } \sqrt[2]{a^2} = +a \text{ or } -a;$$

because there are *two* quantities $+a$, and $-a$, both of which satisfy the condition that, when they are raised to the second power, a^2 results.

(2) Also, given a real quantity a, the operation of division leads to another real quantity. But if we are required to extract the square root of $-a^2$, the operation is impossible, since no real quantity has a negative square. The result must be left as $\sqrt{-a^2}$, or as $a\sqrt{-1}$, or ai, where $i = \sqrt{-1}$. Thus we can say that the problem: "What function is the inverse of a given function?" may or may not have an answer; or it may have more than one answer.

The operation of differentiation, applied to a given function, leads to the differential of that function.

$$\text{Thus } d(x^2) = 2xdx,$$
$$\text{or } d[\phi(x)] = \phi'(x)dx.$$

It is evident that *the operation which is the inverse of differentiation* will be such that, when performed on the differential of a function, it will lead to the function itself. Let us denote this operation by the symbol "∫," then

$$\int dx = x,$$
$$\text{or } \int du = u.$$

"∫" is called the *integral sign;* the operation it denotes is called *integration.* The equation $\int du = u$ may be regarded as defining the meaning of the symbol ∫.

Examples :—

$$\int 2xdx = x^2,$$
$$\int 3x^2dx = x^3,$$
$$\int \frac{dx}{x} = \log x.$$

73. INTEGRATION CONSTANTS

If we put $u = \phi(x)$,
   then $du = \phi'(x)dx$;

and since, by definition,

$$\int du = u,$$
$$\therefore \int\phi'(x)dx = \phi(x) \quad . \qquad . \qquad . \qquad (1)$$

This equation is, however, incomplete. For if C be any arbitrary *constant* whatever, then

$$d(x + C) = dx,$$
$$\text{or } d(u + C) = du ;$$

the arbitrary constant vanishing in the differentiation. Thus

$$\int du = \int d(u + C) = u + C.$$
$$\text{If } u = \phi(x),$$
$$\int\phi'(x)dx = \phi(x) + C \quad . \qquad . \qquad (2)$$

which is the most general definition of $\int$.

C is called the *Integration Constant* ; since its value is, at present, quite arbitrary, the integral $\int\phi'(x)dx$ is called an *indefinite integral*. If, in any particular case, C has a known value, the integral $\int\phi'(x)dx = \phi(x) + C$, is called a *definite integral*.

74. GEOMETRICAL INTERPRETATION

It is easy to find a geometrical interpretation of C. Given a function $\phi'(x)$, the result of integration is a function $\phi(x) + C$. Now $\phi'(x)$ represents the slope or gradient of a curve at a given point $(x = x_1)$, and the operation of integration is that of determining the equation to a curve, i.e. of finding the curve, when the gradient for any value of x between certain limits is known. It is at once obvious that an infinite number of curves may be drawn having the same gradient at every value of x within, it may be, certain limits. The different values of y corresponding to the same value of x may be obtained by the addition (or subtraction) of a constant from any one value.

(i) Let $\dfrac{dy}{dx} = 1$, the curve $y = f(x)$ is obviously *any* straight line making an angle of 45° with the x-axis.

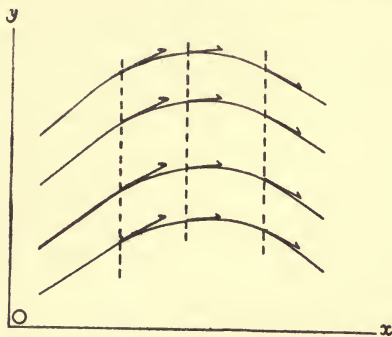The equation $y = x + c$, the integral of $dy = dx$, represents an infinite number of straight lines, one of which

Fig. 24.

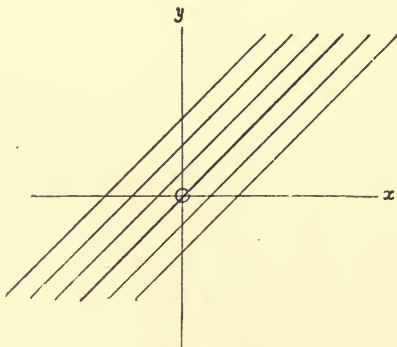passes through the origin and makes an angle of 45° with the x-axis, and all the rest are parallel to this line.

Fig. 25.

The equations of these lines are

$$y = x$$
$$y = x + c_1$$
$$y = x + c_2, \text{ etc.,}$$

and $c_1, c_2 \ldots$ are the lengths of the y-axis cut off by the lines. If $c_1 = 1$, $c_2 = 2$, $\ldots$ the lines are equidistant, as shown in the figure. This family of curves represents the indefinite integral of $\dfrac{dy}{dx} = 1$.

(ii) Another example is the case of a stone falling freely under gravity. If u_0 is the velocity at a given instant, taken as the initial instant, $t = 0$, then the velocity at any time t is given by

$$\frac{ds}{dt} = u_0 + gt,$$

where ds is an element of space, and g is the acceleration of gravity. Integrating, we obtain :—

$$\int ds = \int (u_0 + gt)dt = \int d(u_0 t + \tfrac{1}{2}gt^2) \,;$$
$$\therefore \ s = u_0 t + \tfrac{1}{2}gt^2 + C.$$

Now put $t = 0$,

$\therefore \ s_0 = C$, i.e. C is the distance of the stone from a fixed point at the time we begin observations. If the actual position of the stone at $t = 0$ be taken as this point, $C = 0$.

75. DIFFERENTIATION AND INTEGRATION

We may sum up what has just been said in the statement that, whereas the fundamental proposition of the Differential Calculus is to find the rate of change of a given function, that of the Integral Calculus is to find the function corresponding to a given rate of change :—

$$\text{Function} \quad \overset{\text{Differentiation}}{\underset{\text{Integration}}{\overset{\longrightarrow}{\longleftarrow}}} \quad \text{Rate of Change}$$
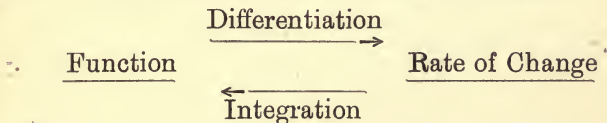
If we remember that the operations denoted by d and $\int$ mutually annul each other, it is clear that if the function to be integrated can be put in the form du, where u is another function, the result of the integration will be

$$u + \text{constant}.$$

Thus $\int 2x\,dx = \int d(x^2) = x^2 + \text{constant.}$

$\quad\int 3x^2\,dx = \int d(x^3) = x^3 + \text{constant.}$

$\quad\int x^4\,dx = \int d\left(\dfrac{x^5}{5}\right) = \dfrac{1}{5}x^5 + \text{constant.}$

$\quad\int\dfrac{dx}{x} = \int d(\log x) = \log x + \text{constant.}$

$\quad\int e^x\,dx = \int d(e^x) = e^x + \text{constant.}$

Integration, as de Morgan said, is "the memory of differentiation". If the function to be integrated does not correspond to any of the standard differentials, it can often be modified so that it does.

76. TABLE OF STANDARD INTEGRALS

(A) $d(x^m) = mx^{m-1}dx$
$\quad \therefore$ if $m = n + 1,$ $\quad\quad \therefore \underline{\int x^n\,dx = \dfrac{1}{n+1}x^{n+1}}$
$d\left(\dfrac{x^{n+1}}{n+1}\right) = x^n dx$

Thus the integrals of x, x^2, x^3, x^{-2}, x^{-5} are $\dfrac{1}{2}x^2$, $\dfrac{1}{4}x^4$, $-\dfrac{1}{x}$, $-\dfrac{1}{4x^4}$.

The case when $n = -1$ is now to be considered.

(B) $d(\log x) = \dfrac{dx}{x} = x^{-1}dx$ $\quad\quad \therefore \underline{\int\dfrac{dx}{x} = \log x.}$

(C) $\quad d(e^x) = e^x dx$ $\quad\quad\quad\quad \underline{\int e^x dx = e^x}$

$\quad\quad d(e^{ax}) = ae^{ax}dx$ $\quad\quad\quad \underline{\int e^{ax}dx = \dfrac{1}{a}e^{ax}}$

$\quad\quad d(a^x) = a^x\log a \,.\, dx$ $\quad\quad \underline{\int a^x dx = \dfrac{a^x}{\log a}.}$

[In all cases, "log" is to be taken as "$\log_e$," unless otherwise indicated.]

The correctness of a result of integration may be tested by differentiating it; the original function should be regained.

77. EXAMPLES

(1) $\int (x + a)^m dx = \int \frac{1}{m + 1} d(a + x)^{m+1}$

$$= \frac{1}{m + 1}(x + a)^{m+1},$$

where a is a *constant*. This is an extension of Type A.

(2) $\quad \int \frac{dx}{x + a} = \log (x + a) ; \int \frac{dx}{x - a} = \log (x - a).$

Examples (1) and (2) show that the *addition* of any arbitrary constant to the variable makes no difference in the *form* of the result.

(3) $\quad \int \frac{dx}{1 - x} = - \int \frac{d(1 - x)}{1 - x} = - \log (1 - x).$

(4) $\quad \int \frac{dx}{a - x} = - \log (a - x).$

(5) $\quad \int \frac{dx}{ax + b} = \frac{1}{a} \int \frac{d(ax + b)}{ax + b} = \frac{1}{a} \log (ax + b).$

(6) $\quad \int \frac{dx}{a - bx} = - \frac{1}{b} \log (a - bx).$

Examples (3) to (6) show that if the variable is *multiplied* by a constant, the integral must be *divided* by that constant. Generally

$$\int f'(kx) dx = \frac{1}{k} f(x).$$

(7) $\qquad \int e^{ax} dx = \frac{1}{a} e^{ax}.$

(8) $\qquad \int e^{-x} dx = - e^{-x}.$

78. TWO GENERAL THEOREMS ON INTEGRATION

(1) $\qquad\qquad \int C du = C \int du \quad . \qquad . \qquad .$ (F)

where C is a constant, u a function of x.

This follows from the definition of $\int$, as is seen by differentiation.

(2) $\int (u + v + w + \ldots) dx = \int u dx + \int v dx + \int w dx + \ldots$
which also follows by differentiation $\quad . \qquad . \qquad .$ (G)

Thus the *Integral of a Sum = sum of integrals of its terms.*

(*a*) An important example is the *rational integral function* of x, i.e. a function of x containing only finite integral powers of x, and in which the denominator is unity. The most general type of such a function is

$$a_0 x^m + a_1 x^{m-1} + a_2 x^{m-2} + \ldots + a_{m-1} x + a_m.$$

m is a positive integer, and the function is *linear, quadratic, cubic*, etc., according as $m = 1, 2, 3$, etc. Generally, it is said to be of the *mth degree* in x.

$$\int (a_0 x^m + a_1 x^{m-1} + a_2 x^{m-2} + \ldots + a_{m-1} x + a_m) dx$$
$$= \frac{1}{m+1} a_0 x^{m+1} + \frac{1}{m} a_1 x^m + \frac{1}{m-1} a_2 x^{m-2} + \ldots$$
$$+ \tfrac{1}{2} a_{m-1} x^2 + a_m x.$$

(*b*) Verify the following results :—

$$\int \left(\frac{1}{x} + x \right) dx = \log x + \frac{1}{2} x^2.$$

$$\int \frac{x+2}{x} dx = x + \log (x^2).$$

79. RATIONAL FRACTIONS

The last example is a special case of the type

$$\frac{\mathrm{F}(x)}{x+a},$$

which is the simplest form of rational fraction. By division

$$\frac{\mathrm{F}(x)}{x+a} = f(x) + \frac{\mathrm{A}}{x+a}, \text{ where}$$

$f(x)$ is a function of x lower in degree by one than $\mathrm{F}(x)$, and A is a constant which is independent of x. Now $f(x)$ must be a rational integral function, which has just been dealt with, and $\frac{\mathrm{A}}{x+a}$ is of the form (B).

Example :—

$$\int \frac{x^2}{1-x} dx = -\frac{1}{2}(x^2 + 2x) - \log (1 - x).$$

(Note: $\int 1 . dx$ is always written $\int dx$; it is, of course, x.)

80. FURTHER GENERAL EXAMPLES

(1) $\quad \displaystyle\int\frac{dx}{2x-1} = \frac{1}{2}\int\frac{d(2x-1)}{2x-1} = \frac{1}{2}\log\,(2x-1).$

$\quad \displaystyle\int\frac{2bx\,dx}{a+bx^2} = \int\frac{d(a+bx^2)}{a+bx^2} = \log\,(a+bx^2).$

Generally, we see that

$$\int\frac{\phi'(x)\,dx}{\phi(x)} = \log\,\phi(x) \qquad\qquad\qquad \text{(I)}$$

Proof :—

$$d[\phi(x)] = \phi'(x)\,dx\,;$$
$$\therefore\ \frac{\phi'(x)\,dx}{\phi(x)} = \frac{d[\phi(x)]}{\phi(x)} = d[\log\,\phi(x)]\,;$$
$$\therefore\ \int\frac{\phi'(x)\,dx}{\phi(x)} = \int d[\log\,\phi(x)] = \log\,\phi(x).$$

This very important rule may be stated in words thus.

If the numerator is the differential of the denominator of the expression, the integral is the natural logarithm of the denominator.

(2) $\quad -\displaystyle\int\frac{dx}{x^n} = \frac{1}{n-1}\cdot\frac{1}{x^{n-1}}$ (Differentiate to prove).

(3) $\quad \int 4x^{-5}dx\,.\,[-x^{-4}].$

(4) $\quad \int 4ax^{-\frac{1}{6}}dn\,.\,[5ax^{\frac{4}{5}}].$

(5) $\quad \int(1+x)^2x^3dx = \int(x^3+2x^4+x^5)dx = (\frac{1}{4}+\frac{2}{5}x+\frac{1}{6}x^2)x^4.$

(6) $\quad \int(a+x^{\frac{1}{2}})^2x^{\frac{1}{2}}dx\,.\,[(\frac{2}{3}a^2+ax^{\frac{1}{2}}+\frac{2}{5}x)x^{\frac{3}{2}}].$

(7) $\quad \displaystyle\int\frac{x\,dx}{1-x^2}\cdot\left[\log\frac{1}{\sqrt{1-x^2}}\right].$

(8) $\quad \displaystyle\int\frac{dx}{x^2-a^2}.$ The denominator is factorisable ;—

$$\frac{1}{x^2-a^2} = \frac{1}{2a}\left\{\frac{1}{x-a}-\frac{1}{x+a}\right\}$$
$$\therefore\quad \int\frac{dx}{x^2-a^2} = \frac{1}{2a}\log\frac{x-a}{x+a}.$$

(9) $\quad \displaystyle\int\frac{dx}{a^2-x^2} = \frac{1}{2a}\log\frac{a+x}{a-x}\,.$ (cf. § 77, ex. 2).

$$(10) \quad \int \frac{dx}{a + bx + cx^2} = \frac{1}{c} \int \frac{d\left(x + \frac{b}{2c}\right)}{\left(x + \frac{b}{2c}\right)^2 - \frac{b^2 - 4ac}{4c^2}}$$

(cf. appendix I)

$$= \frac{1}{(b^2 - 4ac)^{\frac{1}{2}}} \log \frac{2cx + b - (b^2 - 4ac)^{\frac{1}{2}}}{2cx + b - (b^2 - 4ac)^{\frac{1}{2}}} . \tag{J}$$

This result is real only if $b^2 > 4ac$.

$$(11) \quad \int \frac{dx}{a - bx^2} = \frac{1}{b} \int \frac{dx}{\frac{a}{b} - x^2} = \frac{1}{2(ab)^{\frac{1}{2}}} \log \frac{a^{\frac{1}{2}} + b^{\frac{1}{2}}x}{a^{\frac{1}{2}} - b^{\frac{1}{2}}x}.$$

$$(12) \quad \int \frac{dx}{1 - 2x - x^2} = \int \frac{dx}{2 - (x + 1)^2} = \int \frac{d(x + 1)}{2 - (x + 1)^2}$$
$$= \frac{1}{2^{\frac{3}{2}}} \log \frac{2^{\frac{1}{2}} + x + 1}{2^{\frac{1}{2}} - x - 1}.$$

$$(13) \quad \int (a + bx)^n dx = \frac{1}{b} \int (a + bx)^n d(a + bx)$$
$$= \frac{(a + bx)^{n + 1}}{b(n + 1)}.$$

$$(14) \quad \int (a + bx^2)^n x dx = \frac{1}{2b} \int (a + bx^2)^n d(a + bx^2)$$
$$= \frac{(a + bx^2)^{n + 1}}{2b(n + 1)}.$$

$$(15) \quad \int (a^m - x^m)^n x^{m - 1} dx = - \frac{1}{m} \int (a^m - x^m)^n d(a^m - x^m)$$
$$= - \frac{(a^m - x^m)^{n + 1}}{m(n + 1)}.$$

$$(16) \quad \int (a + bx + cx^2)^n (b + 2cx) dx = \frac{(a + bx + cx^2)^{n + 1}}{n + 1}.$$

$$(17) \quad \int \frac{x^2 dx}{(a^3 - x^3)^{\frac{1}{2}}} = - \frac{2}{3}(a^3 - x^3)^{\frac{1}{2}}.$$

81. THE PRINCIPLE OF UNDETERMINED COEFFICIENTS

Two expressions are said to be *identically equal* when they are equal for *all* values of a particular letter in them. The sign $=$ is then often written $\equiv$.

$$\text{E.g. } (a + x)^2 = a^2 + 2ax + x^2,$$

for *all* values of x, or

$$(a + x)^2 \equiv a^2 + 2ax + x^2.$$

A very important theorem concerning such expressions is proved in textbooks on Algebra, viz. the *Principle of Undetermined Coefficients*.

If two functions of a finite number of terms are equal for *all* values of any letter involved in them, then the coefficients of like powers of this letter are equal in the two functions.

Examples :—

(1) Find the square root of $x^4 + 2x^3 + 3x^2 + 2x + 1$.

Let $\sqrt{(x^4 + 2x^3 + 3x^2 + 2x + 1)} \equiv x^2 + mx + 1$,

Then $x^4 + 2x^3 + 3x^2 + 2x + 1 \equiv (x^2 + mx + 1)^2$

$$\equiv x^4 + 2mx^3 + (m^2 + 1)x^2 + 2mx + 1.$$

Equating coefficients of x^3, x^2, and x;

$$2 = 2m, \; 3 = m^2 + 1, \; 2 = 2m,$$

therefore $m = 1$, and

$$\sqrt{(x^4 + 2x^3 + 3x^2 + 2x + 1)} = x^2 + x + 1.$$

(2) If $4x^4 + 8x^3 + mx + n$ is a square, find m and n.

Let $4x^4 + 8x^3 + mx + n \equiv (2x^2 + \mu x + \nu)^2$

$\therefore 4x^4 + 8x^3 + mx + n \equiv 4x^4 + 4\mu x^3 + (\mu^2 + 4\nu)x^2$
$$+ 2\mu\nu x + \nu^2.$$

Then $8 = 4\mu, \; \mu^2 + 4\nu = 0, \; m = 2\mu\nu$

$$\therefore \mu = 2 \; \therefore \nu = -1, \; m = -4$$

$$\therefore n = 1.$$

Confirm by substituting $\mu = 2, \nu = -1, m = -4, n = 1$.

82. PARTIAL FRACTIONS

If a given fraction can be expressed as the sum of two or more fractions, the latter are called its *partial fractions*. Thus $\frac{1}{4}$ and $\frac{1}{5}$ are the partial fractions of $\frac{9}{20}$:—

$$\frac{9}{20} = \frac{1}{4} + \frac{1}{5}.$$

The methods of finding the partial fractions of an algebraic fraction are of great importance in the Integral Calculus. In what follows, the methods will be explained as they arise; further particulars will be found in C. Smith's "Algebra," and Lamb's "Calculus".

83. EQUATIONS OF CHEMICAL KINETICS

(i) *Unimolecular reactions :—*
$$dx/dt = k(a - x).$$

(ii) *Bimolecular reaction :—*
$$dx/dt = k(a - x)(b - x).$$

If $a = b$
$$dx/dt = k(a - x)^2.$$

(iii) *Termolecular reaction :—*
$$dx/dt = k(a - x)(b - x)(c - x).$$

Special cases :—
$$dx/dt = k(a - x)^2(b - x), \ a = c;$$
$$dx/dt = k(a - x)^3; \ a = b = c.$$

In order that these equations may be tested experimentally they must be integrated, because dx/dt cannot usually be found directly (see Introduction).

84. EQUATION OF THE UNIMOLECULAR REACTION

$$dx/dt = k(a - x),$$
$$\therefore \frac{dx}{a - x} = kdt.$$

Integrating we have :—
$$\int \frac{dx}{a - x} - \int kdt = \text{constant} = c,$$
$$\therefore - \log (a - x) - kt = C.$$

C is the unknown arbitrary constant of integration. To determine C we have the experimental relation :—
$$x = 0 \text{ when } t = 0;$$
$$\therefore - \log a = C,$$
$$\therefore \log a - \log (a - x) = kt,$$
$$\text{or } \frac{1}{t} \log \frac{a}{a - x} = k, \ldots$$

which is capable of direct verification.

Instead of determining a, the initial concentration, the equation may be modified so that the concentrations $(a - x_1)$, $(a - x_2)$ at times t_1, t_2 may be used :—

$$kt_1 = - \log (a - x_1) + C,$$
$$kt_2 = - \log (a - x_2) + C,$$
$$\therefore \ k = \frac{1}{t_2 - t_1} \cdot \log\frac{a - x_2}{a - x_1}.$$

The equation may also be thrown into an *exponential form*. Let $a - x = C$, the concentration of active substance at time t ;

$$\therefore \ d(a - x) = - dx = dC ;$$
$$\therefore \ dC/dt = - kC ;$$
$$\text{or } \frac{dC}{C} = - kdt.$$

Integrating we have

$$\log C = - kt + \text{constant}.$$

Put " constant " $= \log b,$
where b is another constant ; and multiply the right-hand member by $\log e = 1$,

$$\log C = \log b - kt \log e$$
$$= \log b + \log e^{-kt}$$
$$= \log be^{-kt}$$
$$\therefore \ \underline{C = be^{-kt}}.$$

This form of integral expresses more clearly the exponential progress of the reaction ; an integral identical in principle with the above was used by Wilhelmy, who made the first application of the law of mass-action.

85. EQUATION OF THE BIMOLECULAR REACTION

$$\frac{dx}{dt} = k(a - x)(b - x),$$

$$\therefore \ \frac{dx}{(a - x)(b - x)} = kdt.$$

The expression $\dfrac{1}{(a - x)(b - x)}$ may be split into Partial Fractions as follows :—

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Assume $\dfrac{1}{(a-x)(b-x)} \equiv \dfrac{A}{a-x} + \dfrac{B}{b-x}$,

which equation must be true for *all* values of x.

Multiply by $(a - x)$:—

$$\frac{1}{b-x} \equiv A + B \cdot \frac{a-x}{b-x}.$$

Put $x = a$,

$$\therefore \frac{1}{b-a} \equiv A;$$

or $A = -\dfrac{1}{a-b}$;

keeping the letters $a, b, c \ldots$ in cyclic order.

Now multiply by $(b - x)$:—

$$\therefore \frac{1}{a-x} \equiv A \cdot \frac{b-x}{a-x} + B.$$

Put $x = b$:—

$$\therefore \frac{1}{a-b} = B;$$

whence the values of A and B are determined.

Thus $\dfrac{1}{(a-x)(b-x)} = \dfrac{1}{a-b}\left\{\dfrac{1}{b-x} - \dfrac{1}{a-x}\right\}$

$$\therefore \int \frac{dx}{(a-x)(b-x)} = \frac{1}{a-b} \cdot \log\frac{a-x}{b-x}.$$

Thus $kt = \dfrac{1}{a-b} \cdot \log\dfrac{a-x}{b-x} + C$,

and by putting $t = 0$ and $x = 0$, we find

$$C = \frac{1}{a-b}\log\frac{b}{a},$$

$$\therefore k = \frac{1}{t(a-b)} \cdot \log\frac{b(a-x)}{a(b-x)}.$$

Exercises ;—

(1) For two times t_1, t_2, prove as in the previous paragraph

$$k = \frac{1}{t_2 - t_1}\log\frac{(a-x_2)(b-x_1)}{(a-x_1)(b-x_2)}.$$

If $a = b$, i.e. reacting substances in equivalent amounts at the start,

$$\frac{dx}{dt} = k(a - x)^2,$$

thence show that

$$ak = \frac{1}{t} \cdot \frac{x}{a - x}.$$

The special case $a = b$ cannot be obtained from the integrated equation by putting $a = b$, since the result is $\frac{1}{t} \cdot \frac{0}{0}$, which is an indeterminate form.

This case will be considered when we are dealing with Taylor's theorem.

(3) If t_1, t_2, are two times, and x_1, x_2 the amounts of change at these times, reckoned from the starting-point, show that :—

$$k = \frac{1}{t_2 - t_1} \cdot \frac{x_2 - x_1}{(a - x_1)(a - x_2)}$$
$$= \frac{1}{t_2 - t_1} \left\{ \frac{1}{a - x_2} - \frac{1}{a - x_1} \right\}.$$

The quantities $(a - x_1)$, $(a - x_2)$ are amounts of substance left unchanged after times t_1, t_2, and are easily found by experiment. This form of the equation, and the corresponding form for the unimolecular reaction, are especially useful when the initial portion of the reaction is disturbed by other simultaneous reactions, as is usually the case. The constant k, deduced from measurements carried out in the initial stages, would therefore be incorrect ; the modified equations enable one to find the constant at any stage in the reaction.

86. EQUATION OF A TERMOLECULAR REACTION

$$dx/dt = k(a - x)(b - x)(c - x),$$
$$\therefore \frac{dx}{(a - x)(b - x)(c - x)} = k\,dt.$$

The expression on the left may be split into three partial fractions :—

$$\frac{1}{(a - x)(b - x)(c - x)} \equiv \frac{A}{a - x} + \frac{B}{b - x} + \frac{C}{c - x}.$$

Multiply each side by $(a - x)$:—

$$\frac{1}{(b - x)(c - x)} \equiv A + (a - x)\left\{\frac{B}{b - x} + \frac{C}{c - x}\right\}.$$

Put $x = a$,

$$\therefore A = -\frac{1}{(a - b)(c - a)}.$$

Similarly, by multiplying by $(b - x)$ and $(c - x)$ and then putting $x = b$, and $x = c$, one finds :—

$$B = -\frac{1}{(a - b)(b - c)} \text{ and } C = -\frac{1}{(b - c)(c - a)}.$$

(Notice the " cyclic order " in the factors.)

Thence we obtain :—

$$\int\frac{dx}{(a - x)(b - x)(c - x)} = -\frac{1}{(a - b)(c - a)}\int\frac{dx}{a - x}$$
$$-\frac{1}{(a - b)(b - c)}\int\frac{dx}{b - x} - \frac{1}{(b - c)(c - a)}\int\frac{dx}{c - x}.$$

Therefore :—

$$\frac{1}{(a - b)(c - a)}\log (a - x) + \frac{1}{(a - b)(b - a)}\log (b - x)$$
$$+ \frac{1}{(b - c)(c - a)}\log (c - x) = kt + \text{constant}.$$

The constant is found as usual by putting $t = 0$, $x = 0$,

$$\therefore C = -\frac{1}{(a - b)(c - a)}\log a - \frac{1}{(a - b)(b - c)}\log b$$
$$-\frac{1}{(b - c)(c - a)}\log c.$$

$$\therefore k = \frac{1}{t} \cdot \frac{\log\left(\frac{a - x}{a}\right)^{(b - c)} . \log\left(\frac{b - x}{b}\right)^{(c - a)} . \log\left(\frac{c - x}{c}\right)^{(a - b)}}{(a - b)(b - c)(c - a)}.$$

Notice the symmetry in the expression.

Exercise :—

If $a = b = c$,

$$\frac{dx}{dt} = k(a - x)^3.$$

Thence prove that

$$k = \frac{1}{2t}\left\{\frac{1}{(a - x)^2} - \frac{1}{a^2}\right\}.$$

87. SPECIAL CASES OF PARTIAL FRACTIONS

(a) Termolecular reaction with *two* equal concentrations.

$$\frac{dx}{dt} = k(a - x)^2(b - x)$$

$$\therefore \frac{dx}{(a - x)^2(b - x)} = kdt.$$

It is proved in advanced textbooks on Algebra (e.g. Chrystal's " Algebra ") that in this case the Partial Fractions are

$$\frac{1}{(a - x)^2(b - x)} \equiv \frac{A}{(a - x)^2} + \frac{B}{a - x} + \frac{C}{b - x}.$$

The student will easily find, in this case, that

$$A = \frac{1}{b - a}, B = -\frac{1}{b - a}, C = -\frac{1}{b - a},$$

and the complete integral is

$$k = \frac{1}{t} \cdot \frac{1}{(b - a)^2} \cdot \left\{\frac{(b - a)x}{a(a - x)} + \log\frac{b(a - x)}{a(b - x)}\right\}.$$

(b) If the denominator contains a quadratic expression which has no real roots we have the following equation for the partial fractions.

Example :—

$$\frac{1}{(x^2 + x + 1)(x - a)(x - b)} \equiv \frac{A}{x - a} + \frac{B}{x - b} + \frac{Cx + D}{x^2 + x + 1},$$

from which the constants may be found by giving x particular values. By way of example, take

$$\frac{1}{(x^2 + x + 1)(x - 1)(x - 2)} \equiv \frac{A}{x - 1} + \frac{B}{x - 2} + \frac{Cx + D}{(x^2 + x + 1)}.$$

Multiplying by $(x^2 + x + 1)(x - 1)(x - 2)$

$$1 \equiv A(x - 2)(x^2 + x + 1) + B(x - 1)(x^2 + x + 1)$$
$$+ (Cx + D)(x - 1)(x - 2).$$

Put $x = 2$:—

$$\therefore 1 \equiv B(2 - 1)(4 + 2 + 1) \therefore B = \tfrac{1}{7}.$$

Put $x = 1 \therefore A = -\tfrac{1}{3}.$

We now substitute the values of A and B in the first of these equations, and give x two values in succession; we can then find C and D by solving the simultaneous equations, preferably by using determinants.

The constants may also be evaluated by equating coefficients of like powers of x, and solving the resulting simultaneous equations.

Example :—

$$\frac{1}{x^4 + x^2 + 1} = \frac{Ax + B}{x^2 + x + 1} + \frac{Cx + D}{x^2 - x + 1}$$

$\therefore 1 \equiv (Ax + B)(x^2 - x + 1) + (Cx + D)(x^2 + x + 1)$

$\therefore 1 \equiv (A + C)x^3 + (- A + C + B + D)x^2$
$$+ (A + C - B + D)x + (B + D).$$

Equating coefficients of like powers of x :—

$$A + C = 0, - A + B + C + D = 0,$$
$$A + C - B + D = 0, B + D = 1.$$

Solving the four equations we get :—

$$A = - C = \tfrac{1}{2}, B = D = \tfrac{1}{2}.$$

(Such cases may often be solved by imaginary substitution, followed by an application of Demoivre's theorem. See Edwards, "Diff. Calculus for Beginners," § 63.)

88. GRAPHICAL METHODS IN CHEMICAL KINETICS

Let C = concentration of a reacting substance; then, by the law of mass-action, the rate at which that substance disappears in the reaction is given by :

$$dC/dt = - kC^n,$$

where n is called the *order* of the reaction.

If more than one substance participates in the reaction,

$$dC/dt = - kC_1^{n_1}C_2^{n_2}C_3^{n_3} \ldots;$$

and the order of the reaction is

$$n = n_1 + n_2 + n_3 + \ldots$$

Van't Hoff identified n with the number of molecules of the reacting substances. Thus in the reaction

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH,$$
$$n = 1 + 1 = 2.$$

Whilst n can usually be defined in this way, there are

cases in which n as derived from velocity measurements does not agree with that derived from the chemical equation, and the former definition is to be preferred. Special cases arise when n is given different values, which of course are integers.

(a) Let $n = 1$, i.e. the reaction is unimolecular,

$$\therefore \; dC/dt = - kC,$$

or the active substance is disappearing at a rate proportional to its concentration at any moment ("compound interest law"). On integration,

$$\frac{dC}{C} = - kdt, \text{ or}$$

$$- \log_e C = kt + \text{constant}.$$

Thus if the logarithms of the concentrations are plotted against times, the graph is a straight line. (Ordinary logarithms may be used, since

$$\log_{10} C = \cdot 4343 \log_e C$$

$$\therefore \; - \log_{10} C = (\cdot 4343k)t + \text{constant}).$$

Values of t and C may also be plotted on semi-logarithmic paper, in which the horizontal rulings are spaced in proportion to the logarithms of the natural numbers. (See Watson, "Text Book of Practical Physics".)

(b) Let $n = 2$, i.e. the reaction is bimolecular,

$$\therefore \; dC/dt = - kC^2$$

$$\therefore \; 1/C = kt + \text{constant}.$$

If reciprocals of concentrations are plotted against times, the graph is a straight line.

The student will easily show that for ter-, quadri-, etc., molecular reactions, $1/C^2$, $1/C^3$, etc., will give straight lines when plotted against t.

Thus, *to find the order of a reaction* we have simply to find by trial which one of the following expressions gives a straight line when plotted against the times :—

    (i) log C (or plot on semi-log-paper) - unimolecular.

    (ii) $1/C$ - bimolecular.

    (iii) $1/C^2$ - termolecular.

    (iv) $1/C^{n-1}$ - n molecular $(n > 1)$,

Any numbers proportional to C may be used, for example the number of c.c. of a standard solution used in titrating the active substance.

A supply of experimental results, for testing the above method, can be found in any textbook of physical chemistry.

89. COURSE OF A REACTION

There is a very important point in connexion with the order of a reaction which may be referred to here, although the full consideration is deferred until later. A large number of chemical reactions appear to be made up of a number of simpler reactions, which may either go on simultaneously (*Side Reactions*), or one after the other (*Consecutive Reactions*). The substance A may be converted into B through an intermediate stage C :—

(i) A → C, followed by the reaction

(ii) C → B.

One of these reactions, say (ii) may be very much faster than the other, and the measured rate is then practically the velocity of (i), the slow reaction. The calculated " order " will then be, not the order of the complete reaction, but that of the slowest component reaction. Prof. James Walker (" Proc. Roy. Soc. Edin.," **22**, 1898) gives a very lucid analogy : " The time occupied by the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram ; but it is obviously this last, slower rate that is of really practical importance in determining the time of transmission ".

The view is becoming more and more pronounced that reactions of higher orders are very rare. These are supposed to be made up of a series of consecutive simpler reactions, and of these the bimolecular reaction appears to be the most frequent. The reason is at once apparent if we consider the subject from the molecular standpoint.

" In illustration, imagine a substance, say gaseous for simplicity, formed by the immediate spontaneous combination of three gaseous components A, B, C. When these gases are mixed, the chances are very remote of the occurrence of the simultaneous triple encounter of an A, a B, and a C, which would be necessary to the immediate formation of an ABC ; whereas if ever formed, it would be liable to the normal chance of dissociating by collisions ; it would thus practically be non-existent in the statistical sense. But if an intermediate combination AB could exist, very transiently, though long enough to cover a considerable fraction of the mean free path of the molecules, this will readily be formed by ordinary binary encounters of A and B, and another binary encounter of AB with C will now form the triple compound ABC in quantity " (Larmor, " Proc. Manchester Phil. Soc.," 1908).

90. REACTION CONSTANTS WITHOUT INTEGRATION

W. C. Bray (" Journ. Phys. Chem. " IX. 573) obtains the reaction constants without integration by the following method. Suppose the equation of the reaction is

$$\frac{dx}{dt} = K(A - x)(B - x)^2.$$

Then we take *any* simple function of A, B, x, t which represents the course of the curve near a point (x, t) for which we require dx/dt, and differentiate it. Thus, in the above equation, if B is large compared with A, we can use

$$\frac{dx}{dt} = k(A - x)$$

to represent a small portion of the curve near (x, t). Then

$$k = \frac{1}{t}ln\frac{A}{A - x} \quad \therefore \quad K = \frac{k}{B^2}.$$

The preliminary constant (k) is calculated from as simple an equation as possible, and the final constant (K) derived from it by means of the differential equation. The value of k must be calculated from pairs of consecutive measurements.

Let k_1 = value of k for (t_1, x_1), $\therefore \dfrac{dx}{dt} = k_1(\mathrm{A} - x_1)$,

$k_2 = $,, ,, (t_2, x_2) $\therefore \dfrac{dx}{dt} = k_2(\mathrm{A} - x_2)$.

But $\dfrac{dx}{dt} = \mathrm{K}\,(\mathrm{A} - x_1)(\mathrm{B} - x_1)^2$,

$\dfrac{dx}{dt} = \mathrm{K}(\mathrm{A} - x_2)(\mathrm{B} - x_2)^2$,

$\therefore \; \mathrm{K} = \dfrac{k_1}{(\mathrm{B} - x_1)^2} = \dfrac{k_2}{(\mathrm{B} - x_2)^2}.$

Chapter IX

THE INDEFINITE INTEGRAL (CONTINUED)

91. HETEROGENEOUS REACTIONS

IF a gas-reaction occurs in a closed vessel, very often a layer of condensed gas is produced on the surface of the vessel, and the amount of gas *adsorbed* in the way is given by

$$x = ap^{\frac{1}{n}},$$

where x = amount of gas adsorbed per unit surface,

p = the pressure,

a, n = constants.

In some cases, a solid is deposited, and this may act catalytically by adsorption. Thus Bodenstein and Stock, in studying the dissociation of stibine,

$$SbH_3 \rightarrow Sb + 3H,$$
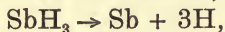
found the deposited antimony to act in this way. If so much antimony is present to begin with, that the deposited amount is, in comparison, negligible, the adsorbing surface may be taken as constant. Assuming the adsorption to take place very rapidly, and only the adsorbed gas to dissociate,

$$-\frac{dx}{dt} = k' \cdot x = k' \cdot ap^{\frac{1}{n}}.$$

But $-dx = -dp$, where dp is the manometric change of pressure (corrected by van der Waals' equation, so as to allow for the " imperfect " nature of stibine)

$$\therefore -\frac{dp}{dt} = k' \cdot ap^{\frac{1}{n}} = kp^{\frac{1}{n}}.$$

Integrating :—

$$k = \frac{1}{\left(1 - \frac{1}{n}\right)\left(t_2 - t_1\right)}\left(p_1^{1 - \frac{1}{n}} - p_2^{1 - \frac{1}{n}}\right).$$

This gave good results with $1/n = 0.6$.

If an inactive solid is deposited on the adsorbing surface during the reaction, the calculation takes a different form. Thus Fink investigated the rate of combination of sulphur dioxide and oxygen on a net of platinum wire as adsorbing surface. The sulphur trioxide forms a layer on this surface, which increases in thickness with progress of the reaction, and the reacting substances have then to *diffuse* through this layer to the adsorbent.

The following statements were assumed by Fink (on the ground of separate experimental results) :—

(1) The velocity of reaction on the surface is very great.

(2) Only the adsorbed gases react.

(3) The oxygen, diffusing more rapidly than sulphur dioxide, will, if the gases are in equivalent proportions, always be in excess on the surface. The after-diffusion of the dioxide is alone of influence on the velocity.

The rate of diffusion is calculated by a very general law due to Fourier, who applied it to the conduction of heat; and extended by Fick, who applied it to the diffusion of a solute through a mass of solvent. It may be given in a general form as follows :—

Rate of diffusion = constant $\times \dfrac{\text{" head " of diffusate}}{\text{thickness of diffusion path.}}$

If the diffusate is heat, the " head " is the difference in temperature between the two faces of the layer of material; the " constant " is the *conductivity* of that material, and the equation assumes the well-known form, for unit area of the layer

$$\frac{Q}{t} = k \cdot \frac{\theta_1 - \theta_2}{\delta},$$

provided $\theta_1 - \theta_2$ remains constant. If this varies

$$\frac{dQ}{dt} = k \cdot \frac{d\theta}{\delta}.$$

If the diffusate is a material substance, spreading through a solvent under the influence of osmotic forces, the "head" of the diffusate is the difference in concentration between two faces of a slice of solution of thickness δ, and the "constant" is the *diffusivity* D. Then

$$\frac{dc}{dt} = D \times \frac{c_1 - c_2}{\delta}, \text{ or}$$

$$\frac{dc}{dt} = D \times \frac{\Delta c}{\delta}.$$

In the case under consideration,

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$\frac{d(2SO_3)}{dt} = k \cdot \frac{D_{SO_2}}{\delta}\left\{ L_{SO_2}(2SO_2)_g - (2SO_2)_w \right\}. \qquad (1)$$

where

$(2SO_2)_g$ = concentration of SO_2 in the gas-space,

$(2SO_2)_w$ = concentration of SO_2 *on* the surface, w,

L_{SO_2} = solubility of SO_2 in the layer

$\therefore L_{SO_2}(2SO_2)_g - (2SO_2)_w$ = head of diffusate.

D_{SO_2} = diffusion-constant of SO_2 through the layer,

δ = thickness of layer (variable);

and, adopting Nernst and Brunner's theory that the velocity of reaction is proportional to the rate at which the reacting material diffuses to the reaction-space, k will be the velocity constant of the chemical reaction.

Considering the layer of constant density, the mass deposited = $w\delta \times$ density = $w\delta\rho$

$$\therefore w\delta\rho = a' \cdot (2SO_3)^{\frac{1}{n}} \text{ by the adsorption law}$$

$$\therefore \delta = \frac{a'}{w\rho}(2SO_3)^{\frac{1}{n}} = a\,(2SO_3)^{\frac{1}{n}}. \qquad (2)$$

Substitute in (1), putting $(2SO_2)_w = 0$ on account of the very great velocity of the surface-reaction,

$$\therefore \frac{d(2SO_3)}{dt} = k_a \cdot \frac{(2SO_2)_g}{(2SO_3)^{\frac{1}{n}}}.$$

Let x = mass of SO_3 produced

a = initial concentration of SO_2

$$\therefore \frac{dx}{dt} = k_a . \frac{(a - x)}{x^{\frac{1}{n}}} \qquad . \qquad . \qquad (3)$$

For most gas-reactions, $1/n = 1/2$ $\therefore$ by substitution in (3) and integration

$$k_a = \frac{1}{t}\left\{a^{\frac{1}{2}}ln\frac{a^{\frac{1}{2}} + x^{\frac{1}{2}}}{a^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}}\right\} \qquad . \qquad . \qquad (4)$$

This was verified by Fink.

If the oxygen is in deficit, so that the sulphur dioxide is now always in excess on the surface, the equation takes the form

$$\frac{d(SO_3)}{dt} = k_b . \frac{(O_2)_g}{(2SO_3)^{\frac{1}{n}}},$$

$$\text{or } \frac{dx}{dt} = k_b . \frac{b - x}{x^{\frac{1}{2}}}.$$

$$\therefore k_b = \frac{1}{t}\left\{b^{\frac{1}{2}}ln\frac{b^{\frac{1}{2}} + x^{\frac{1}{2}}}{b^{\frac{1}{2}} - x^{\frac{1}{2}}} - 2x^{\frac{1}{2}}\right\} \qquad . \qquad . \qquad (5)$$

92. GENERAL EXAMPLES FOR EXERCISE

The following are to be worked by the method of *Partial Fractions*.

(1) $\quad \int\frac{x^3}{1 + x^2}dx = \frac{x^2}{2} - \log \sqrt{1 + x^2}.$

(2) $\quad \int\frac{x^3}{1 - x^2}dx = - \frac{x^2}{2} - \log \sqrt{1 - x^2}.$

(3) $\quad \int\frac{dx}{1 + 3x + 2x^2} = \log\frac{2x + 1}{x + 1}.$

(4) $\quad \int\frac{x + 1}{(x - 1)^2}dx = \log(x - 1) - \frac{2}{x - 1}.$

(5) $\quad \int\frac{xdx}{x^2 + 6x + 8} = \log\frac{(x + 4)^2}{x + 2}.$

(6) $\int\frac{x^2 - 1}{(x-2)(x-3)}dx = x + \log\frac{(x - 3)^8}{(x - 2)^3}.$

The following are to be integrated by the method of *Substitution*.

$$\text{Let } u = f(x),$$
$$du = f'(x)dx.$$

Thus $f(x)$ may be replaced by u, and dx by $\dfrac{du}{f'(x)}$ in the integral. After the integration has been performed, replace the original variable.

(7) $\displaystyle\int \frac{dx}{x(1 + x^2)}.$

$$\text{Put } x^2 = u,$$
$$\therefore \ dx = \frac{du}{2x},$$

$$\therefore \ \int \frac{dx}{x(1 + x^2)} = \tfrac{1}{2}\int \frac{du}{u(1 + u)} = \tfrac{1}{2}\int\left(\frac{1}{u} - \frac{1}{1 + u}\right)du$$
$$= \tfrac{1}{2}\log\frac{u}{1 + u} = \tfrac{1}{2}\log\frac{x^2}{1 + x^2} = \log\frac{x}{\sqrt{1 + x^2}}.$$

(8) $\displaystyle\int \frac{xdx}{x^4 - 1} = \tfrac{1}{4}\log\frac{x^2 - 1}{x^2 + 1}.$

(9) $\displaystyle\int \frac{x^2dx}{(a + bx)^3}.$

$$\text{Put } a + bx = z \quad \therefore \quad x = \frac{z - a}{b};$$

$$bdx = dz \ \therefore \ dx = \frac{dz}{b}.$$

$$\int \frac{x^2dx}{(a + bx)^3} = \int \frac{(z - a)^2}{b^2}\cdot\frac{dz}{bz^3}$$
$$= \frac{1}{b^3}\int \frac{(z - a)^2dz}{z^3}$$
$$= \frac{1}{b^3}\int \frac{z^2 - 2az + a^2}{z^3}dz$$
$$= \frac{1}{b^3}\int\left(\frac{1}{z} - \frac{2a}{z^2} + \frac{a^2}{z^3}\right)dz$$
$$= \frac{1}{b^3}\left(\log z + \frac{2a}{z} - \frac{a^2}{2z^2}\right)$$
$$= \frac{1}{b^3}\left\{\log (a + bx) + \frac{3a^2 + 4abx}{2(a + bx)^2}\right\}.$$

(10) $\int \dfrac{dx}{x^2(a + bx)^2}$.

A double substitution is necessary in this example.

$$\text{Let } x = \frac{1}{z} \therefore dx = -\frac{dz}{z^2}.$$

$$\int \frac{dx}{x^2(a + bx)^2} = -\int \frac{z^2 dz}{(b + az)^2}.$$

Now put $b + az = y$,

$$\therefore z = \frac{y - b}{a},$$

$$dz = \frac{dy}{a}.$$

$$\begin{aligned}
\int \frac{z^2 dz}{(b + az)^2} &= -\int \frac{(y - b)^2}{a^3} \cdot \frac{dy}{y^2} \\
&= -\frac{1}{a^3}\int \frac{(y - b)^2}{y^2} dy \\
&= -\frac{1}{a^3}\int \left(1 - \frac{2b}{y} + \frac{b^2}{y^2}\right) dy \\
&= -\frac{1}{a^3}\left(y - 2b \log y - \frac{b^2}{y}\right) \\
&= \frac{2b}{a^3}\log \frac{a + bx}{x} - \frac{a + 2bx}{a^2 x(a + bx)}.
\end{aligned}$$

(11) $\int \left(a - \dfrac{b}{x^3} + cx^{\frac{3}{2}}\right) dx = ax + \dfrac{b}{2x^2} + \dfrac{2c}{5}x^{\frac{5}{2}}$.

(12) $\int \dfrac{(a - x) dx}{(2ax - x^2)^{\frac{1}{2}}} = (2ax - x^2)^{\frac{1}{2}}$.

(13) $\int \dfrac{\log x}{x} dx = \frac{1}{2}(\log x)^2$.   (Put $x = e^u$.)

(14) $\int \dfrac{(m + nx) dx}{a + bx + cx^2} = \dfrac{n}{2c}\log (a + bx + cx^2)$
$$- \frac{2mc - nb}{2c}\int \frac{dx}{a + bx + cx^2}.$$

(15) Arrhenius used the following expression in his study of the hydrolysis of ethyl acetate:—

$$\frac{1 + mx - nx^2}{(a - x)(b - x)} dx.$$

To integrate, divide out by the denominator

$$\frac{1 + mx - nx^2}{(a - x)(b - x)} = - n + \frac{1 + abn + \{m - n(a + b)\}x}{(a - x)(b - x)}.$$

Put $1 + abn = p$, $m - n(a + b) = q$, p and q being constants. Then assume

$$\frac{p + qx}{(a - x)(b - x)} \equiv \frac{A}{a - x} + \frac{B}{b - x}.$$

By multiplying both sides by $(a - x)(b - x)$, putting $x = a$ and $x = b$ in succession, we readily find ;—

$$A = - \frac{p + aq}{a - b},$$

$$B = \frac{p + bq}{a - b},$$

$$\therefore \int \frac{1 + mx - nx^2}{(a - x)(b - x)} dx = \int \left\{ - n - \frac{p + aq}{a - b} \cdot \frac{1}{a - x} \right.$$
$$\left. + \frac{p + bq}{a - b} \cdot \frac{1}{b - x} \right\} dx$$

$$= - nx + \frac{p + aq}{a - b} \log (a - x) - \frac{p + qb}{a - b} \log (b - x).$$

(16) Noyes' method of finding the order of a chemical reaction is an application of the method of "Equal Fractional Changes". Different initial quantities or concentrations of the reacting substances being taken, the times for the conversion of equal *fractions* of the original amounts are determined. The general velocity equation is

$$- \frac{dC}{dt} = kC^n,$$

$$\text{or} - \frac{dC}{C^n} = kdt.$$

$$\text{Therefore} - \int \frac{dC}{C^n} = kt + \text{const.}$$

In the two experiments let C_1, C_2 be the amounts present at times t_1, t_2. By subtraction, after taking logs ;—

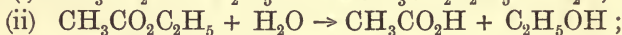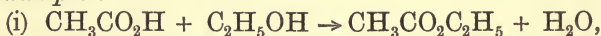$$\log \int \frac{dC}{C_2^n} - \log \int \frac{dC}{C_1^n} = \log t_2 - \log t_1.$$

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By integration, and simplification,

$$\log C_2{}^{n-1} - \log C_1{}^{n-1} = \log t_2 - \log t_1$$
$$\therefore (n-1)(\log C_2 - \log C_1) = \log t_2 - \log t_1$$
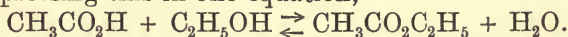$$\therefore n = 1 + \frac{\log t_2 - \log t_1}{\log C_2 - \log C_1}.$$

W. Judson and J. W. Walker applied a similar method to the reaction between hydrobromic and bromic acids (J. C. S., 1898, 410).

(17) In the case of opposing reactions, the products of the direct reaction interact to reproduce the original substances.

Example :—

(i) $CH_3CO_2H + C_2H_5OH \rightarrow CH_3CO_2C_2H_5 + H_2O$,

(ii) $CH_3CO_2C_2H_5 + H_2O \rightarrow CH_3CO_2H + C_2H_5OH$;

or, expressing this in one equation,

$$CH_3CO_2H + C_2H_5OH \rightleftarrows CH_3CO_2C_2H_5 + H_2O.$$

Let a, b, c, d denote the initial concentrations of acid, alcohol, ester, and water ; and let the amount of change after a time t be x.

The velocities of the direct and reverse reactions are

$$\frac{dx_1}{dt} = k_1(a - x)(b - x),$$
$$\frac{dx_2}{dt} = k_2(c + x)(d + x) ;$$

hence the velocity of esterification is

$$\frac{dx}{dt} = \frac{dx_1}{dt} - \frac{dx_2}{dt} = k_1(a - x)(b - x) - k_2(c + x)(d + x).$$

To integrate this equation we put

$$dx/[k(a - x)(b - x) - k_2(c + x)(d + x)] = dt.$$

The denominator on the left can be written

$$(k_1ab - k_2cd) - \{k_1(a + b) + k_2(c + d)\}x + (k_1 - k_2)x^2 ;$$

or dividing by k_2 and putting $k_1/k_2 = K$,

$$(Kab - cd) - \{K(a + b) + (c + d)\}x + (K - 1)x^2 ;$$

which is of the form

$$lx^2 + mx + n.$$

To factorize this expression we proceed as follows :—

Let a, β be the roots of the quadratic equation

$$lx^2 + mx + n = 0.$$

It is proved in the appendix that

$$a = \frac{-m + \sqrt{m^2 - 4ln}}{2l},$$

$$\beta = \frac{-m - \sqrt{m^2 - 4ln}}{2l}.$$

On comparing these results with the expression to be factorized, it is seen that

$$l = K - 1,$$
$$m = -\{K(a + b) + (c + d)\} = -Q \text{ say},$$
$$n = Kab - cd;$$

thence

$$a = \frac{1}{2(K - 1)}\left\{Q + \sqrt{Q^2 - 4(K - 1)(Kab - cd)}\right\},$$

$$\beta = \frac{1}{2(K - 1)}\left\{Q - \sqrt{Q^2 - 4(K - 1)(Kab - cd)}\right\}.$$

Put $\sqrt{Q^2 - 4(K - 1)(Kab - cd)} = P$

$$\therefore a = \frac{Q + P}{2(K - 1)}, \quad \beta = \frac{Q - P}{2(K - 1)}.$$

Thus $(Kab - cd) - \{K(a + b) + (c + d)\}x + (K - 1)x^2$
$$= (x - a)(x - \beta).$$

Now, to split into partial fractions, assume

$$\frac{1}{(x - a)(x - \beta)} = \frac{A}{x - a} + \frac{B}{x - \beta},$$

and, by the usual methods, it is found that
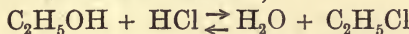
$$A = (K - 1)/P, \quad B = -(K - 1)/P.$$

The expression is now integrable

$$t = \left\{\frac{2(K - 1)^2}{Pk_2}\right\}\left\{\frac{1}{2(K - 1)}\log[2(K - 1)x - (Q + P)]\right.$$
$$\left. - \frac{1}{2(K - 1)}\log[2(K - 1)x - (Q - P)]\right\} + C.$$

To find C_1 put $x = 0$, $t = 0$, and simplify

$$\therefore \frac{1}{t} \cdot \frac{K - 1}{P} \cdot \log\frac{(Q - P)[Q + P - 2(K - 1)x]}{(Q + P)[Q - P - 2(K - 1)x]} = k_2$$

(18) *T. S. Price*, allowing for the autocatalytic effect of the hydrogen ions in the reaction,

$$C_2H_5OH + HCl \rightleftarrows H_2O + C_2H_5Cl$$

obtains $\dfrac{dx}{dt} = k_1(a - x)(b - x)^2 - k_2(c + x)(d + x)(b - x)$.

If no ester is present to begin with, $d = 0$, and

$$\frac{dx}{dt} = k_1\Big\{(a - x)(b - x)^2 - \mathrm{K}x(c + x)(b - x)\Big\},$$

where $k_1/k_2 = \mathrm{K}$.

Integrate in a similar manner to (17), and show that

$$\frac{a + \mathrm{K}c - b(1 - 2\mathrm{K})}{\sqrt{\mathrm{P}}}\log\frac{x\{a + b + \mathrm{K}c - \sqrt{\mathrm{P}}\} - 2ab}{x\{a + b + \mathrm{K}c + \sqrt{\mathrm{P}}\} - 2ab}$$

$$- \log\frac{1}{ab}\Big\{x^2(1 - \mathrm{K}) - x(a + b + \mathrm{K}c) + ab\Big\} + 2\log\frac{b - x}{b}$$

$$= 2\mathrm{K}b(b + c)k_1 t;$$

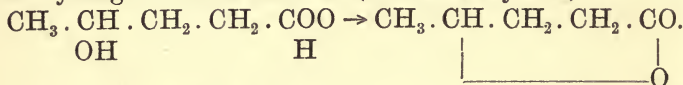where $\mathrm{P} = (a + b + \mathrm{K}c)^2 - 4ab(1 - \mathrm{K})$.

k_2 was found to be only about $\frac{1}{5}k_1$; hence show that, neglecting terms multiplied by k_2,

$$\frac{dx}{dt} = k_1(a - x)(b - x)^2;$$

and $\dfrac{(a - b)x}{b(b - x)} + \log\dfrac{a(b - x)}{b(a - x)} = (a - b)^2 k_1 t.$

(See J. C. S., **79**, 303, 1901.)

(19) *P. Henry* studied the conversion of γ-hydroxy-valeric acid into γ-valerolactone, which is accelerated by the hydrogen ions of the acid ("Autocatalysis").

$$\mathrm{CH_3 . CH . CH_2 . CH_2 . COO} \rightarrow \mathrm{CH_3 . CH . CH_2 . CH_2 . CO.}$$
$$\quad\quad \overset{|}{\mathrm{OH}} \quad\quad\quad \overset{|}{\mathrm{H}} \quad\quad\quad\quad\quad |\underline{\quad\quad\quad\quad\quad}\mathrm{O}$$

Assuming that the rate at which the ring is closed depends upon, and is proportional to

(i) the active mass of the acid,

(ii) the concentration of hydrogen ions derived from it; we get

$$\frac{dx}{dt} = ka(a - x)^2,$$

where a = initial concentration of acid,

$\quad\quad a$ = ionization coefficient of the acid

$$\frac{a^2(a - x)}{1 - a} = \mathrm{K}$$

$$\therefore a = \frac{1}{2(a - x)} \cdot \Big\{\sqrt{4\mathrm{K}(a - x) + \mathrm{K}^2} - \mathrm{K}\Big\}.$$
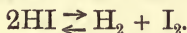
Put $4K(a - x) + K^2 = P^2$,
$$\therefore a - x = (P^2 - K^2)/4K$$
$$dx = - PdP/2K.$$

Split into partial fractions, put $\sqrt{4Ka - K^2} = Q$, integrate as in (17), and we get

$$\frac{1}{t}\left\{\frac{Q - P}{(P - K)(Q - K)} + \frac{1}{2K}\log\frac{(P + K)(Q - K)}{(P - K)(Q + K)}\right\} = k.$$

(20) *M. Bodenstein* studied the rate of decomposition of hydriodic acid heated in a glass bulb. Let 1 gram molecule of HI be heated in a v litre globe.

$$2HI \rightleftarrows H_2 + I_2.$$
$$\frac{dx}{dt} = k_1\left(\frac{1 - 2x}{v}\right)^2 - k_2\left(\frac{x}{v}\right)^2,$$

where $\dfrac{1 - 2x}{v}$ = concentration of undissociated acid.

Put $k_1/k_2 = K$
$$\therefore \int\frac{dx}{K(1 - 2x)^2 - x^2} = k_2t/v^2.$$

Put $\dfrac{1}{K(1 - 2x)^2 - x^2} \equiv \dfrac{A}{\sqrt{K}(1 - 2x) + x} + \dfrac{B}{\sqrt{K}(1 - 2x) - x}$,

$$\therefore 1 \equiv (2\sqrt{K} + 1)A\left(\frac{\sqrt{K}}{2\sqrt{K} + 1} - x\right)$$
$$+ (2\sqrt{K} - 1)B\left(\frac{\sqrt{K}}{2\sqrt{K} - 1} - x\right).$$

Putting $x = \dfrac{\sqrt{K}}{2\sqrt{K} - 1}$, and $\dfrac{\sqrt{K}}{2\sqrt{K} + 1}$ in succession,
$$A = \frac{-2\sqrt{K} - 1}{2\sqrt{K}}, \ B = \frac{2\sqrt{K} + 1}{2\sqrt{K}}.$$

The student will now complete the integration.

$$\frac{1}{2\sqrt{K}}\log\frac{\sqrt{K}(1 - 2x) + x}{\sqrt{K}(1 - 2x) - x} = k_2t/v^2.$$

(21) Integrate $\dfrac{5x^3 + 1}{x^2 - 3x + 2}$ by partial fractions.

$$\left[\frac{5x^2}{2} + 15x - 6\log(x - 1) + 41\log(x - 2).\right]$$

(22) Integrate $\dfrac{9x^2 + 9x - 128}{x^3 - 5x^2 + 3x + 9}$ by partial fractions.

$$\left[- 8 \log (x + 1) + \frac{5}{x - 3} + 17 \log (x - 3). \right]$$

(23) Integrate $\dfrac{x^2 + 1}{(x - 1)^4 (x^3 + 1)}$.

Assume $\dfrac{x^2 + 1}{(x-1)^4 (x^3 + 1)} = \dfrac{A_1}{(x-1)^4} + \dfrac{A_2}{(x-1)^3} + \dfrac{A_3}{(x-1)^2}$
$$+ \frac{A_4}{(x-1)} + \frac{Cx + D}{x^2 - x + 1} + \frac{B}{x + 1},$$

$\therefore x^2 + 1 = \{A_1 + A_2(x - 1) + A_3(x - 1)^2 + A_4(x - 1)^3\}(x^3 + 1)$
$\quad + \{B(x^2 - x + 1) + (Cx + D)(x + 1)\}(x - 1)^4$.   (1)

$$\text{Put } x = 1 \therefore 2 = 2A_1 \quad . \quad . \quad . \quad (2)$$
$$\therefore A_1 = 1.$$

From (1) and (2) by subtraction

$x^2 - 1 = A_1(x^3 - 1) + \{A_2 + A_3(x - 1) + A_4(x - 1)^2\} \ldots$
$\quad \times (x - 1)(x^3 + 1) + \{B(x^2 - x + 1) + (Cx + D)(x + 1)\}(x-1)^4.$

Divide by $x - 1$, then

$x + 1 = A_1(x^2 + x + 1) + \{A_2 + A_3(x - 1) + A_4(x - 1)^2\}$
$\quad \times (x^3 + 1) + \{B(x^2 - x + 1) + (Cx + D)(x + 1)\}(x - 1)^3$ (3)

$$\text{Put } x = 1, \text{ then } 2 = 3A_1 + 2A_2. \quad . \quad (4)$$
$$\therefore A_2 = - \tfrac{1}{2}.$$

We subtract (3) and (4), divide by $x - 1$, put $x = 1$, etc., and so on, until we have found A_1, A_2, A_3, A_4, B_1, C_1 and D. The separate fractions are then integrated, and the result is

$$- \frac{1}{3(x - 1)^3} + \frac{1}{4(x - 1)^2} + \frac{1}{4(x - 1)} + \frac{5}{8}\log (x - 1)$$
$$+ \tfrac{1}{24} \log (x + 1) - \tfrac{1}{3} \log (x^2 - x + 1).$$

93. INTEGRATION OF IRRATIONAL FUNCTIONS

An irrational function may be transformed into a rational function of a new variable by suitable substitution. For the general discussion, see Lamb's "Calculus," §§ 75, 85. We shall indicate the nature of the process by the consideration of particular examples.

Examples :—

(1) $\int x \sqrt{1 + x} \, . \, dx$.

$$\text{Substitute } x + 1 = u^2,$$
$$\therefore x = u^2 - 1,$$
$$\therefore dx = 2u\,du.$$

$$\begin{aligned}
\int x \sqrt{1 + x} \, . \, dx &= \int (u^2 - 1)2u^2 du \\
&= 2\int u^4 du - 2\int u^2 du \\
&= \tfrac{2}{5}u^5 - \tfrac{2}{3}u^3 \\
&= \tfrac{2}{5}(x + 1)^{\frac{5}{2}} - \tfrac{2}{3}(x + 1)^{\frac{3}{2}} \\
&= 2(x + 1)^{\frac{3}{2}} \left\{ \frac{x}{5} - \frac{2}{15} \right\}.
\end{aligned}$$

(2) $\displaystyle\int \frac{dx}{x \sqrt{1 + x}}$, by the same substitution as (1), gives

$$\begin{aligned}
\int \frac{dx}{x \sqrt{1 + x}} &= 2\int \frac{u\,du}{(u^2 - 1)u} = 2\int \frac{du}{u^2 - 1} \\
&= \log\frac{u - 1}{u + 1}, \text{ by Partial Fractions,} \\
&= \log\frac{\sqrt{1 + x} - 1}{\sqrt{1 + x} + 1}.
\end{aligned}$$

(3) $\displaystyle\int \frac{dx}{x \sqrt{5 - 6x^5}}$.

$$\text{Put } x^5 = \frac{1}{u^2}$$
$$\therefore 5 \log x = - 2 \log u$$
$$\therefore \frac{5}{x}dx = - \frac{2}{u}du$$
$$\text{or } \frac{dx}{x} = - \frac{2}{5} \cdot \frac{du}{u}.$$

$$\begin{aligned}
\int \frac{dx}{x \sqrt{5 - 6x^5}} &= - \frac{2}{5}\int \frac{du}{u\sqrt{5 - \dfrac{6}{u^2}}} \\
&= - \frac{2}{5}\int \frac{du}{\sqrt{5u^2 - 6}} \\
&= - \frac{2}{5\sqrt{5}}\int \frac{du}{\sqrt{u^2 - \dfrac{6}{5}}}.
\end{aligned}$$

Now

$$d[\log (x + \sqrt{x^2 \pm a^2})] = \frac{dx}{\sqrt{x^2 \pm a^2}},$$

hence the last integral is

$$= - \frac{2}{5\sqrt{5}}\log \left(u + \sqrt{u^2 - \frac{6}{5}}\right).$$

The substitution of $x^{-\frac{5}{2}}$ for u will complete the integration.

(4) $\int \dfrac{dx}{\sqrt{x^2 + a^2}}$

may be independently worked as follows—a very instructive example :—

$$\text{Let } a^2 + x^2 = z^2,$$
$$\therefore\ xdx = zdz,$$
$$\therefore\ \frac{dz}{z} = \frac{dx}{x} = \frac{dx + dz}{x + z},$$

by the very important rule of the Theory of Proportion, viz. if a series of fractions are equal,

$$\text{each fraction} = \frac{\text{sum of numerators}}{\text{sum of denominators}}.$$

Proof :—

$$\text{Let } \frac{dz}{z} = \frac{dx}{x} = k.$$

Then $dz = kz$, and $dx = kx$,
$\therefore\ (dx + dz) = k(x + z)$,

$$\frac{dx + dz}{x + z} = k = \frac{dz}{z} = \frac{dx}{x}.$$

Hence $\int \dfrac{dx}{\sqrt{a^2 + x^2}} = \int \dfrac{dz}{z} = \int \dfrac{dx + dz}{x + z} = \int \dfrac{d(x + z)}{x + z}$
$$= \log (x + z) = \log \{x + \sqrt{a^2 + x^2}\}$$

(5) $\int \dfrac{dx}{\sqrt{x^2 - a^2}} = \log \{x + \sqrt{x^2 - a^2}\}$

(6) $\int \dfrac{dx}{x\sqrt{a^2 - x^2}} = \int \dfrac{dx}{x^2\left(\dfrac{a^2}{x^2} - 1\right)^{\frac{1}{2}}} = - \dfrac{1}{a}\int \dfrac{d\left(\dfrac{a}{x}\right)}{\left(\dfrac{a^2}{x^2} - 1\right)^{\frac{1}{2}}}$

$$= -\frac{1}{a}\log\left\{\frac{a}{x} + \left(\frac{a^2}{x^2} - 1\right)^{\frac{1}{2}}\right\}$$

$$= \frac{1}{a}\log\frac{x}{a + \sqrt{a^2 - x^2}}.$$

(7) A double substitution is required in integrating

$$\int\frac{dx}{x^4\sqrt{x^2 - 1}}.$$

Put $x = 1/z$,

$$\therefore \log x = -\log z$$
$$\therefore dx/x = -dz/z$$
$$x^2 - 1 = 1/z^2 - 1 = (1 - z^2)/z^2$$

$$\therefore \int\frac{dx}{x^4(x^2 - 1)^{\frac{1}{2}}} = -\int\frac{z^2\dfrac{dz}{z}}{\dfrac{(1 - z^2)^{\frac{1}{2}}}{z}} = \int\frac{z^2(-zdz)}{(1 - z^2)^{\frac{1}{2}}}.$$

Now substitute $1 - z^2 = u^2$

$$\therefore -2zdz = 2udu,$$
$$\text{or} -zdz = udu.$$
$$\text{Also } z^2 = 1 - u^2$$

$$\therefore \int\frac{z^2(-zdz)}{(1 - z^2)^{\frac{1}{2}}} = \int\frac{(1 - u^2)udu}{u} = \int(1 - u^2)du$$

$$= u - \frac{u^3}{3} = u\left(\frac{3 - u^3}{3}\right)$$

$$= \frac{\sqrt{1 - z^2}}{3}\left(3 - 1 + z^2\right)$$

$$= \frac{\sqrt{x^2 - 1}}{3x}\left(2 + \frac{1}{x^2}\right)$$

$$= \frac{2x^2 + 1}{3x^3}\sqrt{x^2 - 1}.$$

(8) Integrate

$$\int\frac{dx}{x^4\sqrt{1 + x^2}}.$$

Put $1 + x^2 = z^2x^2.$ $\quad\left[\dfrac{(2x^2 - 1)(1 + x^2)^{\frac{1}{2}}}{3x^3}.\right]$

94. METHODS OF APPROXIMATE INTEGRATION

It may be proved that every *continuous* function has an indefinite integral. This integral may not, however, be expressible in a finite form by using the ordinary functions of mathematics.

Examples :—

$$\int e^{x^2}dx, \int \frac{e^{ax}}{x} dx, \int \frac{dx}{\sqrt{1 + x^3}}$$

cannot be integrated in finite terms, because we do not know any ordinary function which, when differentiated, gives as a result e^{x^2}, etc. Now such integrals often occur in practical work. Thus $\int e^{-x^2}dx$ is a very important integral in physics, occurring in the mathematical treatment of heat conduction (Fourier's theorem), the secular cooling of the earth, the kinetic theory of gases, and the path of a ray of light through a continuously varying medium. Two lines of attack suggest themselves.

(1) *Invent a new mathematical function.*

Thus, if we had been ignorant of the logarithmic function, we could not have integrated the expression $\int \frac{dx}{x}$, and such a function might have been suggested by an attempt to integrate this particular expression. (Cf. Hardy's "Course of Pure Mathematics," Cambridge, 1908, chap. IX.) Various new functions have arisen in this way; for example Legendre's Elliptic Functions, the Error Function, etc.

(2) *Obtain an approximate value of the integral.*

The method most generally employed is to endeavour to express the function as an infinite convergent series, which may then be capable of integration to any desired degree of accuracy. This is called *Integration by Series*.

Let $y = \phi(x)$

be the function we are given to integrate.

Assume that $\phi(x)$ may be expressed in the form of an infinite convergent series :—

$$\phi(x) = a_0 + a_1x + a_2x^2 + \ldots + a_nx^n + \ldots$$

When we assume that a function can be expanded into such a series, containing only algebraic terms, we assume that it is a continuous function.

The constants a_0, a_1, a_2, ..., which are independent of the value x, are at present undetermined. If these constants can be found up to a certain point in the series, the value of the integral can be at once found to a degree of accuracy corresponding to the magnitude of the terms of the series which have been rejected. The integral is in fact

$$\int \phi(x)\,dx = a_0 x + \frac{1}{2}a_1 x^2 + \frac{1}{3}a_2 x^3 + \ldots + \frac{1}{n+1}a_n x^{n+1} + \ldots$$

The investigation of the next paragraph enables us to find the values of the constants a_0, a_1, a_2, ... in the series.

95. MACLAURIN'S THEOREM

Maclaurin's Theorem determines the law for the expansion of a function of a *single variable* in terms of a series of ascending powers of that variable.

$$\text{Let } u = \phi(x),$$

and *assume* that $\phi(x)$ can be developed into a series of ascending powers of x, this series being uniformly convergent. Then the derivative $\phi'(x)$ may be obtained by differentiating the series term by term :—

$$\phi(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_n x^n + \ldots$$
$$\therefore \phi'(x) = a_1 + 2a_2 x + \ldots + n a_n x^{n-1} + \ldots$$

The resulting series will also be convergent, and the process of differentiation may be repeated.

$$\phi''(x) = 2a_2 + \ldots + n(n-1)a_n x^{n-2} + \ldots$$
$$\phi'''(x) = 2.3.a_3 + \ldots + n(n-1)(n-2)a_n x^{n-3} + \ldots$$
$$\ldots\ldots$$
$$\phi^n(x) = n(n-1)(n-2)\ldots3.2.1.a_n + \ldots;$$

a constant vanishing at each step. With the "factorial" notation $(2! = 1.2; \; 3! = 1.2.3,$ etc.; $n! = n(n-1)\ldots 2.1)$:—

$$\phi(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \ldots + a_nx^n + \ldots$$
$$\phi'(x) = a_1 + 2a_2x + 3a_3x^2 + \ldots + na_nx^{n-1} + \ldots$$
$$\phi''(x) = 2!\ a_2 + 3!a_3x + \ldots + n(n-1)a_nx^{n-2} + \ldots$$
$$\cdots\cdots$$
$$\phi^n(x) = n!\ a_n + \ldots$$

These equations being true for all values of x, the constants $a_0, a_1, a_2, \ldots a_n$ have the same value for a particular form of $\phi(x)$ whatever value we assign to x. Let us assaume that $x = 0$:—

$$\phi(0) = a_0 \qquad\qquad \therefore\ a_0 = \phi(0)\ ;$$
$$\phi'(0) = a_1 \qquad\qquad \therefore\ a_1 = \phi'(0)\ ;$$
$$\phi''(0) = 2!\ a_2 \qquad\qquad \therefore\ a_2 = \frac{1}{2!}\phi''(0)\ ;$$
$$\phi'''(0) = 3!\ a_3 \qquad\qquad \therefore\ a_3 = \frac{1}{3!}\phi'''(0)\ ;$$
$$\cdots\cdots$$
$$\phi^n(0) = n!\ a_n \qquad\qquad \therefore\ a_n = \frac{1}{n!}\phi^n(0).$$

$\phi(0)$, $\phi'(0)$, etc. imply that x is put equal to 0 *after* the differentiations have been performed. Substituting the values of $a_0, a_1, \ldots a_n$, we get

$$\phi(x) = \phi(0) + x\phi'(0) + \frac{x^2}{2!}\phi''(0) + \ldots + \frac{x^n}{n!}\phi^n(0) + \ldots$$

which is called *Maclaurin's Theorem.*

96. TAYLOR'S THEOREM

Let $u = \phi(x + y)$.

Taylor's theorem determines the law for the expansion of a *sum or difference of two variables* in terms of a series of ascending powers of *one variable*.

We *assume* that

$$\phi(x + y) = a_0 + a_1y + a_2y^2 + \ldots + a_ny^n + \ldots$$

where $a_0, a_1, a_2, \ldots$ are independent of y, but may be functions of x. Now since the series is assumed to be true for all values of x and y, it will be true when x assumes a particular value ξ.

$$\phi(\xi + y) = a'_0 + a'_1y + a'_2y^2 + \ldots + a'_ny^n + \ldots$$

Put $z = \xi + y$, $\therefore\ y = z - \xi$, and, by Maclaurin's theorem

$$u' = \phi(z) = a'_0 + a'_1(z - \xi) + a'_2(z - \xi)^2 + \ldots + a_n(z - \xi)^n + \ldots$$
$$\phi'(z) = \qquad a'_1 \qquad + 2a'_2(z - \xi) + 3a'_3(z - \xi)^2 + \ldots$$
$$\phi''(z) = \qquad\qquad 2 \cdot a'_2 \qquad + 3 \cdot 2 \cdot a'_3(z - \xi) + \ldots$$
$$\phi'''(z) = \qquad\qquad\qquad 3 \cdot 2 \cdot a'_3$$
$$\qquad\qquad\qquad\qquad + 4 \cdot 3 \cdot 2 \cdot a_4(z - \xi) + \ldots .$$

Maclaurin's theorem deduces the values of $a_0, a_1, \ldots$ on the hypothesis that $x = 0$, but in the present case it is required that $x = \xi$. Let $z = \xi$ $\therefore\ y = (z - \xi) = 0$,

$$\phi(\xi) = a'_0 \qquad\qquad \therefore\ a'_0 = \phi(\xi) ;$$
$$\phi'(\xi) = a'_1 \qquad\qquad \therefore\ a'_1 = \phi'(\xi) ;$$
$$\phi''(\xi) = 2\,!\,a'_2 \qquad\qquad \therefore\ a'_2 = \frac{1}{2\,!}\phi''(\xi) ;$$
$$\phi'''(\xi) = 3\,!\,a'_3 \qquad\qquad \therefore\ a'_3 = \frac{1}{3\,!}\phi'''(\xi) ;$$
$$\cdots \qquad\qquad\qquad \cdots$$
$$\phi^n(\xi) = n\,!\,a'_n \qquad\qquad \therefore\ a'_n = \frac{1}{n\,!}\phi^n(\xi) ;$$

$$\therefore\ \phi(\xi + y) = \phi(\xi) + \phi'(\xi)y + \phi''(\xi)\frac{y^2}{2\,!} + \phi'''(\xi)\frac{y^3}{3\,!} + \ldots$$
$$+ \phi^n(\xi)\frac{y^n}{n\,!} + \ldots$$

But ξ being any value of x, we put $\xi = x$,

$$\therefore\ u = \phi(x + y) = \phi(x) + \phi'(x)y + \phi''(x)\frac{y^2}{2\,!} + \phi'''(x)\frac{y^3}{3\,!} + \ldots$$
$$+ \phi^n(x)\frac{y^n}{n\,!} + \ldots$$

which is *Taylor's Series*.

97. EXAMPLES ON MACLAURIN'S THEOREM

(1) $\qquad\qquad$ Let $u = (a + x)^n$
$\phi(x) = (a + x)^n \qquad\qquad \therefore\ \phi(0) = a^n ;$
$\phi'(x) = n(a + x)^{n-1} \qquad\qquad \therefore\ \phi'(0) = na^{n-1} ;$
$\phi''(x) = n(n - 1) \cdot (a + x)^{n-2} \quad \therefore\ \phi''(0) = n(n - 1)a^{n-2} ;$
and so on. Substitute in Maclaurin's series :—

$$(a + x)^n = a^n + na^{n-1} \cdot x + n(n - 1)a^{n-2}\frac{x^2}{2\,!} + \ldots$$

which is the well-known *Binomial Series*.

Now this is true for *positive integral values of n for all values of x*; but if n is *negative* or *fractional*, the expansion fails unless x *lies between* ± 1. In the latter case the assumption virtually made on expansion into a series is invalid, i.e. $\phi(x)$ cannot be expanded into a convergent power series.

(*a*) Integrate $(1 + x)^{\frac{2}{3}}$ in series.

$$(1 + x)^{\frac{2}{3}} = 1 + \tfrac{2}{3}x - \tfrac{1}{9}x^2 + \tfrac{4}{81}x^3 - \ldots$$

$$\therefore \int(1 + x)^{\frac{2}{3}}dx = x + \tfrac{1}{3}x^2 - \tfrac{1}{27}x^3 + \tfrac{1}{81}x^4 - \ldots$$

Now if $x = 0.1$, say,

$x^4 = 0.00001$, and $\tfrac{1}{81}x^4 = 0.000001$ approximately.

The remaining terms are still less, and it will probably be sufficient to stop after the fourth term.

(*b*) The coefficient of expansion of a gas, liquid, or solid, is defined by the equation

$$V_t = V_0(1 + at),$$

where V_0, V_t = volumes at $0°$ C., $t°$ C., and a is the coefficient of expansion. This equation may be written

$$V_t = V_0 + at.$$

where $a = V_0 a$ = constant.

Let m, ρ be the mass and density of a given amount of the substance, then $m = \rho V$,

$$\therefore \rho_0/\rho_t = V_t/V_0 = 1 + at,$$
$$\therefore \rho = \rho_0/(1 + at),$$
$$= \rho_0(1 + at)^{-1},$$
$$= \rho_0(1 - at + (at)^2 - (at)^3 + \ldots)$$

by Maclaurin's theorem.

In the case of mercury, $a = 0.00018$; in the case of air $a = 0.0036$.

Thence show that if ρ is required to be accurate to 6 decimal places, all terms after the second may be neglected in the case of mercury, but not in the case of air.

(*c*) $\displaystyle\int\frac{dx}{(1 - x^2)^{\frac{1}{2}}} = x + \frac{1}{2.3}x^3 + \frac{1.3}{2.4.5}x^5 + \ldots$

(*d*) $\int(1 + x^2)^{-1}dx = x - \tfrac{1}{3}x^3 + \tfrac{1}{5}x^5 - \ldots$

(2)
$$\text{Let } u = e^x,$$
$$\text{then } e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

(a) If $u = a^x$,
$$u = 1 + x \cdot \log a + \frac{x^2}{2!}(\log a)^2 + \dots$$

(b) If $u = e^{-x}$, show that
$$u = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots$$

(c) $\int e^{-x^2} dx = x - \dfrac{x^3}{1 \cdot 3} + \dfrac{x^5}{1 \cdot 2 \cdot 5} - \dfrac{x^7}{1 \cdot 2 \cdot 3 \cdot 7} + \dots$

(d) $\phi(x) = \log (1 + x)$.
$$\phi(x) = \log (1 + x) \qquad \therefore \ \phi(0) = 0$$
$$\phi'(x) = \frac{1}{1 + x} \qquad\qquad \therefore \ \phi'(0) = 1$$

and so on,

$$\therefore \ \phi(x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \dots$$

Also show that if
$$\phi(x) = \log (1 - x),$$
$$\phi(x) = - x - \tfrac{1}{2}x^2 - \tfrac{1}{3}x^3 - \dots$$

These are convergent only if $x < 1$.

98. EXAMPLES ON TAYLOR'S THEOREM

(1)
$$\text{Let } u_1 = (x + y)^n.$$
Put $y = 0 \ \therefore \ u = x^n$;
$$\phi(x) = x^n;$$
$$\phi'(x) = ux^{n-1};$$
$$\phi''(x) = n(n - 1)x^{n-2}; \text{ etc.}$$

But $u_1 = \phi(x) + \phi'(x) \cdot y + \phi''(x) \cdot \dfrac{y^2}{2!} + \dots$

$$= x^n + nx^{n-1} \cdot y + n\frac{(n - 1)}{2!}x^{n-2}y^2 + \dots$$

(2) Let $u_1 = a^{x+y}$
$$= a^x \cdot a^y.$$

Put $y = 0$, $u = a^x$;

$\phi(x) = a^x$;

$\phi'(x) = a^x \log a$;

$\phi''(x) = a^x (\log a)^2$; and so on.

Thus $u_1 = \phi(x + y)$

$$= a^x\left(1 + y . \log a + \frac{y^2}{2!}\left(\log a\right)^2 + \frac{y^3}{3!}\left(\log a\right)^3 + \ldots\right).$$

(3) Let $u_1 = e^{x + h}$.

$$u_1 = e^x + he^x + \frac{h^2}{2!}e^x + \frac{h^3}{3!}e^x + \ldots$$

(4) Let $u_1 = (x + y + a)^{\frac{1}{2}}$.

$$u_1 = (x + a)^{\frac{1}{2}} + \tfrac{1}{2}(x + a)^{-\frac{1}{2}} . y. \ldots$$

Examine the case $x = - a$.

(5) Let $u_1 = \log (x + y)$.

$$u_1 = \log x + \frac{y}{x} - \frac{y^2}{2x^2} + \frac{y^3}{3x^3} - \ldots$$

(6) Let $u = \log (n + h)$;

where h is small compared with n, and $h < 1$.

$$\log (n + h) = \log n + \frac{h}{n} - \frac{h^2}{2n^2} + \ldots$$

If $h < 1$ and $n = 10000$, $\dfrac{h}{n} < 0.0001$,

$$\frac{h^2}{2n^2} < 0.000,000,005, \text{ which is quite negligible.}$$

$$\text{Hence } \log (n + h) = \log n + \frac{h}{n};$$

$$\text{and } \log (n + 1) = \log n + \frac{1}{n}.$$

Thence $\dfrac{\log (n + h) - \log n}{\log (n + 1) - \log n} = \dfrac{h}{1}$,

the familiar "Rule of Proportional Parts" in logarithms.

(7) $\log \dfrac{1 + x}{1 - x} = 2\left\{\dfrac{x}{1} + \dfrac{x^3}{3} + \dfrac{x^5}{5} + \ldots\right\}$.

This can be used to find log N, where $N > 1$, if $N = \dfrac{1 + x}{1 - x}$.

99. SOME EXAMPLES ON INFINITE INTEGRALS

(1) The velocity equation for a bimolecular reaction is
$$dx/dt = k(a - x)(b - x).$$

The integral of this has been shown to be
$$k = \frac{1}{t} \cdot \frac{1}{a - b} \cdot \log \frac{b(a - x)}{a(b - x)} \qquad . \qquad . \qquad (1)$$

If $a = b$, this reduces to
$$k = \frac{1}{t} \cdot \frac{1}{0} \cdot \log 1 = \frac{1}{t} \cdot \frac{0}{0}.$$

The fraction $\frac{0}{0}$ is "indeterminate". The case $a = b$ may, however, be developed by an application of Maclaurin's theorem.

$$\text{For } a - x = a\left(1 - \frac{x}{a}\right),$$
$$b - x = b\left(1 - \frac{x}{b}\right),$$
$$\therefore \log \frac{(a - x)b}{(b - x)a} = \log \frac{(1 - x/a)}{(1 - x/b)} = \log\left(1 - \frac{x}{a}\right) - \left(1 - \frac{x}{b}\right)$$

Develop the logarithms by the logarithmic series (example 2(d) on Maclaurin's theorem) :—

$$\log (1 - x/a) = - \left\{\frac{x}{a} + \tfrac{1}{2} \frac{x^2}{a^2} + \tfrac{1}{3} \frac{x^3}{a^3} + \ldots\right\},$$
$$\log (1 - x/b) = - \left\{\frac{x}{b} + \tfrac{1}{2} \frac{x^2}{b^2} + \tfrac{1}{3} \frac{x^3}{b^3} + \ldots\right\},$$

whence
$$\log \frac{(a - x)b}{(b - x)a} = x\left(\frac{1}{b} - \frac{1}{a}\right) + \frac{x^2}{2}\left(\frac{1}{b^2} - \frac{1}{a^2}\right) + \frac{x^3}{3}\left(\frac{1}{b^3} - \frac{1}{a^3}\right) + \ldots$$
$$= x\frac{a - b}{ab} + \frac{x^2}{2} \frac{a^2 - b^2}{a^2b^2} + \frac{x^3}{3} \frac{a^3 - b^3}{a^3b^3} + \ldots$$
$$= (a - b)\left\{\frac{x}{1} \cdot \frac{1}{ab} + \frac{x^2}{2} \cdot \frac{a + b}{a^2b^2} + \frac{x^3}{3} \cdot \frac{a^2 + ab - b^2}{a^3b^3} + \ldots\right\}$$

Now substitute in (1), and $(a - b)$ cancels :—
$$\frac{1}{a - b}\log \frac{b(a - x)}{a(b - x)} = \frac{x}{1} \cdot \frac{1}{ab} + \frac{x^2}{2} \cdot \frac{a + b}{a^2b^2} + \frac{x^3}{a^3} \cdot \frac{a^2 + ab - b^2}{a^3b^3} + \ldots$$

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Put $a = b$,

$$\underset{a \to b}{\text{Lim}} \left[\frac{1}{a - b} \log \frac{b(a - x)}{a(b - x)} \right] = \frac{x}{a^2} + \frac{x^2}{a^3} + \frac{x^3}{a^4} + \dots$$

$$= \frac{x}{a^2} \left(1 + \frac{x}{a} + \frac{x^2}{a^2} + \dots \right)$$

$$= \frac{x}{a^2} \cdot \frac{1}{\left(1 - \dfrac{x}{a} \right)} = \frac{x}{a(a - x)},$$

on summing the geometrical series. Thus

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)},$$

which has been found independently by integrating the equation

$$dx/dt = k(a - x)^2.$$

(2)   If $dx/dt = k(a - x)(b - x)^2$,

find the integral when a is very nearly equal to b.

Add and subtract $(b - x)^{-3}$:—

$$dx/(a - x)(b - x)^2$$

$$= \left[\frac{1}{(b - x)^3} + \frac{1}{(a - x)(b - x)^2} - \frac{1}{(b - x)^3} \right] dx$$

$$= \left[\frac{1}{(b - x)^3} - \frac{a - b}{b - x} \left\{ \frac{1}{(b - x)^3} - \frac{a - b}{b - x} \cdot \frac{1}{(a - x)(b - x)^2} \right\} \right] dx$$

$$= \left[\frac{1}{(b - x)^3} - \frac{a - b}{(b - x)^4} + \frac{(a - b)^2}{(b - x)^5} - \frac{(a - b)^3}{(b - x)^6} + \dots \right] dx$$

a geometrical series which is convergent if $(a - b) < (b - x)$, which may be satisfied by taking a sufficiently near b, before developing into a series. Integrate term by term :—

$$k = \frac{1}{t} \left[\frac{1}{2} \left\{ \frac{1}{(b - x)^2} - \frac{1}{b^2} \right\} - \frac{a - b}{3} \left\{ \frac{1}{(b - x)^3} - \frac{1}{b^3} \right\} + \dots \right]$$

If a is nearly equal to b, all terms after the first bracket may be neglected :—

$$k = \frac{1}{2t} \left[\frac{1}{(b - x)^2} - \frac{1}{b^2} \right],$$

a result which is independent of a.

(3)
$$\int \frac{e^{ax}}{x} dx$$

cannot be integrated in finite terms.

$$e^{ax} = 1 + ax + \frac{a^2 x^2}{1 \cdot 2} + \frac{a^3 x^3}{1 \cdot 2 \cdot 3} + \dots,$$

$$\frac{e^{ax}}{x} = \frac{1}{x} + a + \frac{a^2 x}{1 \cdot 2} + \frac{a^3 x^3}{1 \cdot 2 \cdot 3} + \dots,$$

$$\int \frac{e^{ax}}{x} dx = \log x + ax + \frac{a^2 x^2}{1 \cdot 2 \cdot 2} + \frac{a^3 x^3}{1 \cdot 2 \cdot 3 \cdot 3} + \dots,$$

a result which will be required later.

(4)
$$\int \frac{e^x}{x^2} dx.$$

Let $e^x = v, \ -1/x = u,$

$$\therefore \ dv = e^x, \ du = \frac{1}{x^2}.$$

Now we have by the result of the differential calculus

$$d(uv) = v du + u dv,$$
$$\therefore \ \int d(uv) = \int v du + \int u dv,$$
$$\therefore \ \int v du = uv - \int u dv.$$

Comparing with the values of u and v selected, we see that

$$\int \frac{e^x}{x^2} dx = -\frac{e^x}{x} + \int \frac{e^x}{x} dx$$
$$= -\frac{e^x}{x} + \log x + x + \frac{x^2}{1 \cdot 2 \cdot 2} + \frac{x^3}{1 \cdot 2 \cdot 3 \cdot 3} + \dots$$

This is an example of " Integration by Parts ".

(5) $\int \frac{e^{2x} - 1}{e^{2x} + 1} dx$

may be integrated in finite terms by a suitable transformation.

$$e^{2x} - 1 = e^x \left(e^x - \frac{1}{e^x} \right) = e^x (e^x - e^{-x}),$$
$$e^{2x} + 1 = e^x \left(e^x + \frac{1}{e^x} \right) = e^x (e^x + e^{-x}).$$

$$\int \frac{e^{2x} - 1}{e^{2x} + 1} dx = \int \frac{e^x - e^{-x}}{e^x + e^{-x}} = \int \frac{d(e^x + e^{-x})}{e^x + e^{-x}} = \log (e^x + e^{-x}).$$

(6) $\int e^{e^x} e^x dx = e^{e^x},$

since $de^{e^x} = e^x dx.$

(7) $\int \dfrac{e^x x dx}{(1+x)^2} = \int \left\{ \dfrac{e^x}{1+x} - \dfrac{e^x}{(1+x)^2} \right\} dx$

$\qquad\qquad = \int \dfrac{1}{1+x} d(e^x) + \int e^x d\left(\dfrac{1}{1+x}\right)$

$\qquad\qquad = \dfrac{2e^x}{1+x}.$

Chapter X

DEFINITE INTEGRALS

100. THE DEFINITE INTEGRAL

THE process of integration we have so far considered merely as the inverse of differentiation; so that if $\phi'(x)$ be the differential coefficient of a function, the problem of integration has been to find $\phi(x)$, the function from which $\phi'(x)$ was derived. Another very important meaning which may be attached to integration is to regard it as the process of finding the *limiting value of a sum*, when the terms tend to become infinitely small, and their number infinitely large. We will consider the matter from a geometrical point of view.

FIG. 26.

Let the line $OR_0 = x_0$ be increased continuously from x_0 to $OR_n = x_n$, say by the uniform motion of a particle placed in the line. Let R_1, R_2 be two successive positions of the advancing point very close together. Describe squares on OR_0, OR_1, OR_2, OR_n.
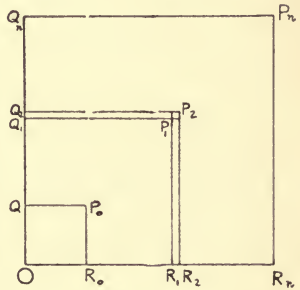
$$\text{Let } R_1R_2 = dx,$$
$$\tfrac{1}{2}(R_1P_1 + R_2P_2) = x,$$
$$\therefore \text{ gnomon } Q_2P_1R_2 = 2x\,dx.$$

As P_0 advances along OP_n, whilst R_0 advances along OR_n, the figure Q_nR_n is formed continuously from the infinitesimal gnomons like Q_2R_2, and the total area is the sum of these when their size is diminished indefinitely.

$$\text{Area} = \Sigma 2x\,dx \text{ when } dx \to 0$$
$$= \text{Lim } \Sigma 2x\,dx\,;$$
$$dx \to 0$$

and to indicate that the summation is to extend over a range from $x = x_0$ to $x = x_n$, we write this

$$\underset{dx \to 0}{\text{Lim}} \sum_{x=x_0}^{x=x_n} 2x\,dx.$$

This symbol we shall now abbreviate to

$$\int_{x_0}^{x_n} 2x\,dx\,;$$

which is called the *Definite Integral* of $2x$ between the *limits of integration* $x = x_0$ and $x = x_n$. (Note the difference in meaning between "limit of integration," and "limit" as used up to this point.)

$$\text{But area} = OQ_nP_nR_n - OQ_0P_0R_0$$
$$= x^2_n - x^2_0$$
$$= \int^x d(x^2).$$

The definite integral is therefore equal to the difference between the values of the indefinite integrals when $x = x^n$ and $x = x_0$:—

$$\int_{x_0}^{x_n} 2x\,dx = x^2_n - x^2_0\,;$$
$$\text{also } \int 2x\,dx = x^2 + C$$
$$\therefore \text{ if } x = x_n, \text{ this } = x^2_n + C\,;$$
$$\text{if } x = x_0, \text{ this } = x^2_0 + C\,;$$

the difference being $x^2_n - x^2_0$.

This is denoted by

$$\left[x^2\right]_{x_0}^{x_n} = x^2_n - x^2_0\,;$$

the square brackets indicating that the value for $x = x_0$ is to be subtracted from the value for $x = x_n$.

We shall now extend this reasoning.

101. THE DEFINITE INTEGRAL

Let $y = f'(x)$

be a function of x which is finite and continuous from $x = x_0$ to $x = x_n$.

Let the range $x_n - x_0$ be subdivided into a large number of small intervals $x_1 - x_0, x_2 - x_1, \ldots x_n - x_{n-1}$. Erect ordinates from $x_0, x_1, \ldots$ to the curve, and draw inner and outer rectangles as shown.

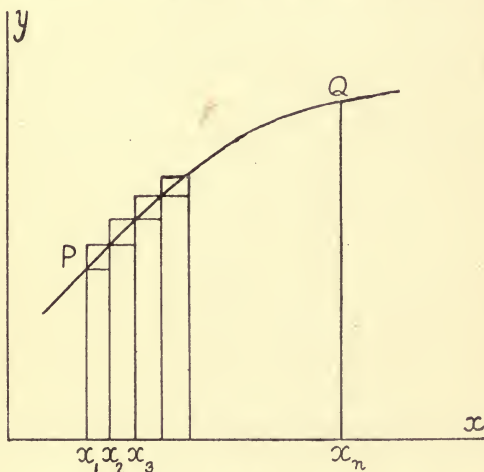If $x_1 - x_0 = x_2 - x_1 = \ldots = x_n - x_{n-1} = \delta x$, the differ-

FIG. 27.

ence between the sums of the outer and the inner rectangular areas is

$$(y_n - y_0)\,\delta x;$$

which can be made as small as we please by increasing the number of intervals and decreasing their size. Each sum therefore approaches the same finite limit when dx is diminished indefinitely and this is defined as the area enclosed by the curve, the extreme ordinates $x = x_0$ and $x = x_n$, and the axis of x.

The sum of the inner rectangles is

$$f'(x_0)\delta x + f'(x_1)\delta x + \ldots + f'(x_{n-1})\delta x$$
$$= f'(x_0)\delta x + f'(x_0 + \delta x)\delta x + f'(x_0 + 2\delta x)\delta x + \ldots$$
$$= \sum_{r=0}^{r=n-1} f'(x_0 + r\delta x)\delta x.$$

We define the limiting value of this sum, when $\delta x \to 0$, and

$$n\delta x = x_n - x_0,$$

as the *area* enclosed by the curve, and denote it by

$$\int_{x_0}^{x_n} f'(x)\,dx.$$

Now, considering any small strip, say that on $x_3 x_4$, we have, if δA is its area, $y_4 \delta x > \delta A > y_3 \delta x$. But as δx is diminished y_3 and y_4 approach each other continuously, and in the limit we may write

$$dA_n = y_n dx;$$
$$\therefore \int dA_n = \int y_n dx;$$
$$\text{or } A_n = \int y_n dx + C$$
$$= \int f'_n(x)\,dx + C.$$

Let $f(x)$ be a function such that

$$\int f'(x)\,dx = f(x) + C;$$
$$\text{then } A_n = f(x_n) + C,$$
$$\text{where } A_n = \text{area } PQx_n x_0.$$

If $x_n = x_0$, this area vanishes

$$\therefore 0 = f(x_0) + C,$$
$$\text{or } C = -f(x_0),$$
$$\therefore \int_{x_0}^{x_n} f'(x)\,dx = f(x_n) - f(x_0).$$

The reason for the symbol of integration in

$$\int_{x_0}^{x_n} f'(x)\,dx$$

is now apparent; the definite integral being the difference between the indefinite integrals at the limits of integration. The name " definite integral " is used because the arbitrary constant of integration vanishes when the integration is performed between definite limits,

102. EXAMPLES ON THE DEFINITE INTEGRAL

(1) Find the area enclosed by the part of the parabola
$$y^2 = 4ax,$$
the ordinates at $x = x_1$, $x = x_2$, and the axis of x.

We imagine the area divided up into very narrow strips such as P_1x_1. The sum of the areas of these strips, when their width is indefinitely diminished, and their number indefinitely increased, is the required area.

$$\text{Area of strip } P_1x_1 = y_1 dx$$
$$\text{But } y = 2\sqrt{ax},$$
$$\therefore \text{ area of strip } = 2\sqrt{ax_1} . dx.$$
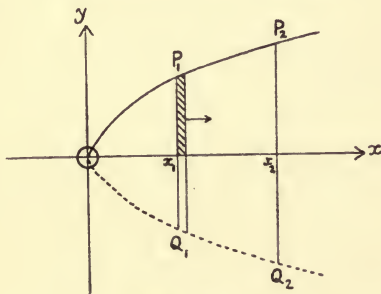
FIG. 28.

Total area $P_1P_2x_2x_1$ = limit of sum of strips such as Px_1 when their thickness is reduced indefinitely

$$= \int_{x_1}^{x_2} 2\sqrt{ax}\, dx$$
$$= 2\sqrt{a}\int_{x_1}^{x_2} x^{\frac{1}{2}} dx$$
$$= 2\sqrt{a}\left[\frac{2}{3}x^{\frac{3}{2}}\right]_{x_1}^{x_2} = \frac{4}{3}a^{\frac{1}{2}}\left(x_2^{\frac{3}{2}} - x_1^{\frac{3}{2}}\right).$$

(The area $P_1P_2Q_2Q_1$ is *twice* this area.)

(2) The area enclosed between the curve
$$y = ax^n,$$
the axis of x, and the ordinate $x = \xi$ is

$$\int_0^\xi y dx = \int_0^\xi x^n dx$$
$$= a\left[\frac{1}{n+1}x^{n+1}\right]_0^\xi$$
$$= \frac{a}{n+1}\xi^{n+1}.$$

If $a\xi^n$ = length of extreme ordinate = η,

$$\text{area} = \frac{\xi\eta}{n+1}.$$

(3) Area enclosed between the rectangular hyperbola
$$xy = c,$$
the x-axis, and $x = a$, $x = b$ can be easily shown to be
$$c \log \frac{b}{a}.$$

(4) Prove that
$$\int_a^b e^{ax} dx = \frac{1}{a}\left(e^{ab} - e^{aa}\right).$$

(5) Find the area between the ordinates $x = 1$, $x = 4$, of the parabola $y^2 = 4x$. [Area = $9\frac{1}{3}$ sq. cm.]
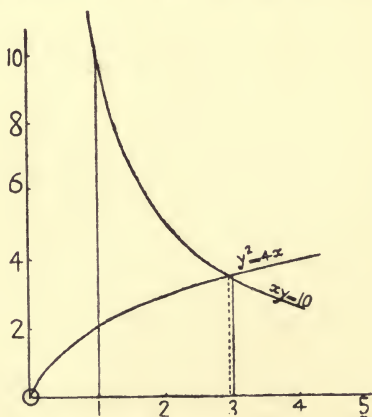
FIG. 29.

(6) Find the area enclosed between
the parabola $y^2 = 4x$,
the hyperbola $xy = 10$,
and the ordinates $x = 1$, $x = 3$.

On solving the equations $y^2 = 4x$, $xy = 10$, for x we find that the parabola and hyperbola cut at $x = 2.92$. We have therefore to find the area under the hyperbola from the point $x = 1$ to the point $x = 2.92$; the area under the parabola between the same limits, and then subtract the second area from the first. We then find the areas from $x = 2.92$ to $x = 3$, subtract the area under the hyperbola from the area under the parabola, and add the result to the first difference. Thus required area

$$= \left\{ \int_1^{2.92} \frac{10}{x} dx - \int_1^{2.92} \sqrt{4x} dx \right\} - \left\{ \int_{2.92}^3 \sqrt{4x} dx - \int_{2.92}^3 \frac{10}{x} dx \right\}$$

$$= 10 \log_e 2.92 - \{\tfrac{4}{3}((2.92)^{\frac{3}{2}} - 1^{\frac{3}{2}})\}$$
$$\qquad\qquad - \{\tfrac{4}{3}(3^{\frac{3}{2}} - (2.92)^{\frac{3}{2}}) - 10(\log_e 3 - \log_e 2.92)\}$$

$$= 10 \log_e 3 - \tfrac{4}{3}(3^{\frac{3}{2}} - 1^{\frac{3}{2}})$$

$$= 10.986 - 5.594$$

$$= \underline{5.392 \text{ sq. cm.}}$$

(7) Find the area enclosed by the curve

$$y = e^{-2x}$$

between the ordinates $x = 1$ and $x = 2$.

$$\text{Area} = e^{-4} - e^{-2}$$
$$= \frac{1}{e^4} - \frac{1}{e^2} = \frac{e^2 - 1}{e^4} = 0.117.$$

(8) Find the area enclosed between the curve $y = x^2$, the straight line $y = 2 - x$, and the ordinate $x = 0.5$.

Draw the graphs of the curves.

The line cuts the curve in two points, the co-ordinates of which are obtained by solving the equations:—

$$y = x^2$$
$$y = 2 - x$$
$$\therefore \ x^2 + x - 2 = (x + 2)(x - 1) = 0,$$
$$\text{i.e. } x = -2 \text{ or } x = +1.$$

The required area will be one of two areas seen in the figure.

(i) If $x = + 1$,

area under the line $= \dfrac{y_1 + y_2}{2}(x_2 - x_1) = \dfrac{1 - 5 + 1}{2} \times \cdot 5$
$$= \underline{\cdot 625.}$$

area under the curve $= \left[\dfrac{1}{3}x^3\right]_{\cdot 5}^{1} = \underline{\cdot 291.}$

The difference of areas is therefore
$$0\cdot 625 - 0\cdot 291 = \underline{0\cdot 334 \text{ sq. units.}}$$
        (ii) If $x = - 2$,

area under the line $= \dfrac{4 + 1\cdot 5}{2} \times 2\cdot 5 = \underline{6\cdot 875 \text{ sq. units.}}$

The area under the curve now consists of two parts, that for $x = 0$ to $x = + 0\cdot 5$, and that for $x = - 2$ to $x = 0$;

$$\therefore \text{ area } = \left[\dfrac{1}{3}x^3\right]_{0}^{0.5} + \left[\dfrac{1}{3}x^3\right]_{0}^{2} = \left[\dfrac{1}{3}x^3\right]_{0}^{2.5},$$

neglecting signs, $= \underline{5\cdot 208 \text{ sq. units.}}$

The required area is thus $6\cdot 875 - 5\cdot 208 = \underline{1\cdot 667 \text{ sq. units.}}$

These results should be verified by plotting the curves on squared paper and counting up the enclosed squares.

103. SOME PROPERTIES OF THE DEFINITE INTEGRAL

(1) $$\int_{b}^{a}\phi(x)dx = - \int_{a}^{b}\phi(x)dx,$$

since the " increments " dx are now negative.

(2) If the integral area lies wholly above or below the x-axis in the part considered, and if
$$\phi(- x) = \phi(x) ;$$
i.e. $\phi(x)$ is an *even* function of x ;
$$\int_{-a}^{+a}\phi(x)dx = 2\int_{o}^{a}\phi(x)dx ;$$
the first integral being bisected by the axis of y.

E.g. $\phi(x) = x^2, x^4, x^6$, etc.

(3) But if $\phi(- x) = - \phi(x)$; i.e. $\phi(x)$ is an *odd* function of x ;

$$\int_{-a}^{+a} \phi(x)dx = 0;$$

because in forming the sum, every element of area $\phi(x)dx$ is cancelled by the element $\phi(-x)dx$ of opposite sign.
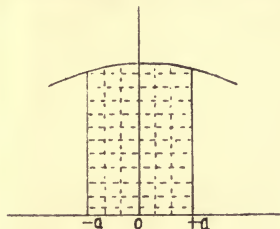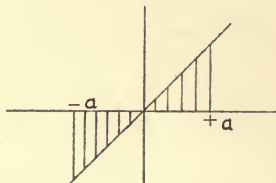

FIG. 30.

FIG. 31.

E.g. if $y = \phi(x) = x$,
$$\phi(x) = x, \quad \phi(-x) = -x$$
$$\int_{-a}^{+a} x\,dx = \tfrac{1}{2}a^2 - \tfrac{1}{2}a^2 = 0.$$

(4) If part of the curve, or all the curve, lies below the axis of x, the corresponding definite integral is *negative*,
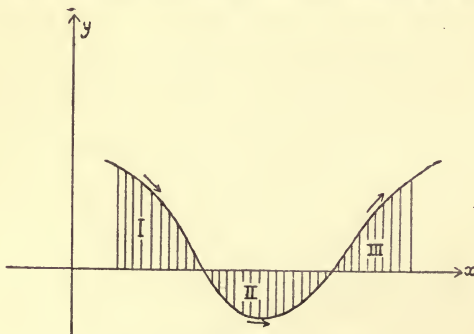

FIG. 32.

since the values of $\phi(x)$ used in forming the sum are negative. If the curve cuts the x-axis at points x_1, x_2, . . . part of the area lies above and part below the x-axis. In this case we integrate separately up to these points and

add the areas. The integral taken over the whole range gives the *algebraic* sum of the areas. In the figure

$$\int_{x_1}^{x_4} y\, dx = (\text{I}) - (\text{II}) + (\text{III}).$$

(5) $$\int_a^b \phi'(x)\, dx = \int_a^m \phi'(x)\, dx + \int_m^b \phi'(x)\, dx.$$

This is seen from the figure, or analytically

$$\int_a^b \phi'(x)\, dx = \phi(b) - \phi(a) \quad . \quad . \quad . \quad \text{(i)}$$

$$\int_m^b \phi'(x)\, dx = \phi(b) - \phi(m) \quad . \quad . \quad . \quad \text{(ii)}$$

$$\int_a^m \phi'(x)\, dx = \phi(m) - \phi(a) \quad . \quad . \quad \text{(iii)}$$

∴ since (ii) + (iii) = (i) the proposition is proved. (Compare with Example 8 of the preceding section.)

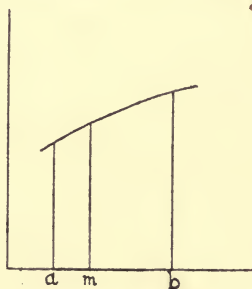
Fig. 33.

104. INTEGRATION BY PARTS

Integration by Parts is a method of integration of very great service in dealing with expressions containing exponential or trigonometrical functions, and it is often required in the applications to physical chemistry. It is used when the function to be integrated is the *product of two functions, one of which is a differential coefficient.*

$$\text{E.g. } \int x \log x\, dx = \int (\log x) \frac{d}{dx}\left(\frac{x^2}{2}\right).$$

The method is an inversion of the very important formula of the Differential Calculus

$$d(uv) = udv + vdu.$$

Integrating both sides

$$uv = \int udv + \int vdu$$

Special case :

$$v = x$$
$$ux = \int udx + \int xdu.$$
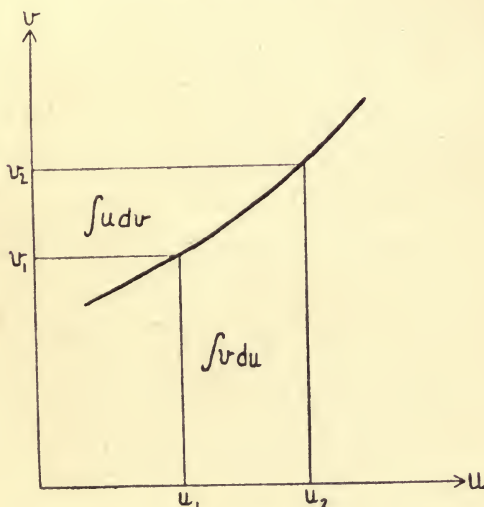

Fig. 34.

Now in many cases, one of the integrals $\int udv$, $\int vdu$, is more easily obtained than the other. Suppose this is $\int vdu$. Then

$$\int udv = uv - \int vdu ;$$

i.e. from the product of the two factors subtract the integral of the non-integrated factor with respect to the integrated factor.

The factor which is a differential (v) must be picked out by trial; the progress of the integration will soon

indicate whether the correct factor has been chosen or not

Graphically, the total shaded area represents

$$uv = (u_2 - u_1)(v_2 - v_1),$$

considering the definite integral

$$\left[uv \right]_1^2.$$

The area above the curve is

$$\int_{v_1}^{v_2} u\, dv,$$

that below the curve is

$$\int_{u_1}^{u_2} v\, du.$$

Obviously $uv = \int v\, du + \int u\, dv$.

(Note that v is the independent variable in the first case, u that in the second.)

105. EXAMPLES ON INTEGRATION BY PARTS

(1) $\int x^2 e^{ax}\, dx$.

It is obvious on inspection that $e^{ax} = \dfrac{1}{a} d(e^{ax})$,

hence, following the method explained above, we set

$$\left. \begin{array}{l} dv = e^{ax} dx \\ v = \dfrac{1}{a} e^{ax} \end{array} \right\} \left. \begin{array}{l} u = x^2 \\ du = 2x\, dx \end{array} \right\}.$$

Then by the formula

$$\int x^2 e^{ax} = \frac{1}{a} x^2 e^{ax} - \frac{1}{a} \int e^{ax} \cdot 2x \cdot dx.$$

We have now to deal with the second integral on the right.

$$\left. \begin{array}{l} \text{Put } dv = e^{ax} dx \\ v = \dfrac{1}{a} e^{ax} \end{array} \right\} \left. \begin{array}{l} u = 2x \\ du = 2\, dx \end{array} \right\}$$

$$\int 2x e^{ax} dx = \frac{1}{a} e^{ax} \cdot 2x - \frac{2}{a} \int e^{ax} dx$$

$$= \frac{2}{a} x e^{ax} - \frac{2}{a^2} e^{ax}.$$

Therefore $\int x^2 e^{ax} dx = \frac{1}{a} x^2 e^{ax} + \frac{2}{a} x e^{ax} - \frac{2}{a^2} e^{ax}$

$$= \frac{e^{ax}}{a}\left(x^2 - \frac{2x}{a} - \frac{2}{a^2}\right).$$

Suppose that, instead of e^{ax}, we had chosen x^2 as the differential, i.e. $d\left(\dfrac{x^3}{3}\right)$.

$$\left.\begin{array}{c} v = \dfrac{x^3}{3} \\ dv = x^2 dx \end{array}\right\} \quad \left.\begin{array}{c} u = e^{ax} \\ du = a e^{ax} dx \end{array}\right\}$$

$$\therefore \int x^2 e^{ax} dx = \frac{x^3}{3} e^{ax} - \frac{a}{3}\int x^3 e^{ax} dx.$$

The result is a more complicated integral than the one we started with, indicating that our choice of the differential factor was not suitable.

(2) $\int x \log x\, dx = \frac{1}{2} x^2 (\log x - \frac{1}{2})$.

(3) $\int x e^x dx = (x - 1)e^x$.

(4) $\int \log x\, dx = x (\log x - 1)$.

This is an important case. Note that $u = 1$.

(5) $\int x^{-1} dx = \int x^{-1} \partial x$.

(6) $\displaystyle\int \frac{\log x}{x} dx = \frac{1}{2}(\log x)^2$.

(7) $\displaystyle\int \frac{dx}{(a^2 - x^2)^2} = \frac{x}{2a^2(a^2 - x^2)} + \frac{1}{4a^3}\log\frac{a + x}{a - x}$.

Chapter XI

APPLICATIONS OF THE DEFINITE INTEGRAL

106. THE EXPANSION OF GASES

(i) LET 1 gram molecule of a perfect gas be enclosed in an imaginary cylinder, fitted with an airtight piston sliding without friction. Let the whole be placed in a vacuous space, and the piston loaded with weights until it is in equilibrium.

Let p = pressure on piston (per unit area). The equation connecting the variables is

$$pv = RT \text{ (Horstmann's equation)};$$

where v = volume (22·24 litres), T = absolute temperature, R is the gas-constant.

Now suppose the pressure on the piston ever so slightly diminished by taking off a very small weight, say a milligram. The gas expands slightly, until the new volume corresponds to the slightly diminished pressure. The work done = force × distance

$$\therefore dA = p \times \text{(area of piston)} \times \text{(movement of piston)}$$
$$\therefore dA = pdv,$$

where dv is the slight increase of volume.

The curve representing the expansion is a rectangular hyperbola, T being supposed kept constant, and the work done by a finite expansion from volume v_1 to volume v_2 is given by

$$\int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} \frac{RT}{v} \cdot dv = RT \int_{v_1}^{v_2} \frac{dv}{v}$$
$$= RT \int_{v_1}^{v_2} d (\log v)$$
$$= RT (\log v_2 - \log v_1)$$
$$= RT \log \frac{v_2}{v_1}.$$

To show that "log" means "natural logarithm," we often write it " ln " :—

$$\therefore \text{ work done } = A = RT\ln\frac{v_2}{v_1}.$$

If we had n gram molecules of gas in the cylinder instead of one,

$$pv = nRT,$$
$$\text{and } A_n = nRT\ln\frac{v_2}{v_1}.$$

The work done *on* the gas by compression is $-RT\ln\frac{v_2}{v_1}$.

Examples :—

(1) Show that $A = RT\ln\frac{p_1}{p_2}$.

(2) Interpret the two expressions for the work by means of the diagram expressing p as a function of v.

(3) Show that $\int pdv = -\int vdp$ if the gas obeys Boyle's law.

107. ISOTHERMAL AND REVERSIBLE EXPANSION.

We have considered the expansion to be effected in a cylinder under a piston; it will next be shown that the work is the same no matter how the gas expands from volume v_1 to volume v_2, provided two conditions are satisfied.

Consider any mass of gas confined, for example, in an elastic envelope subjected to a uniform pressure p all over its surface. Let its volume be v_1. Now imagine a slight expansion,

FIG. 35.

shown by the dotted perimeter, to take place consequent upon a slight diminution of pressure.

The total (small) increase of volume, between the full and dotted perimeters, may be imagined divided into a large number of small cylinders, such as A, in each of

which the increase of volume is Δv. The work done is $\Sigma p \Delta v = p \Sigma \Delta v = p dv$, where dv is the increase of volume taken over the *whole* surface.

Hence in every case of expansion, under the conditions specified, from an initial volume v_1 to a final volume v_2, the work done is

$$A = RT \ln \frac{v_2}{v_1}.$$

The conditions are:—

(1) The temperature T remains constant. This may be ensured by immersing the cylinder in a large tank of water at temperature T, and performing the expansions and compressions so slowly that any heat absorbed or produced is compensated by conduction from or to the heat reservoir. The case is one of *Isothermal expansion*.

(2) The pressure of the gas is just balanced at every instant by the pressure due to the load on the piston. A very slight increase of pressure causes the piston to move down instead of up, the expansion changes to a compression, and the process is reversed. A process is said to be conducted *reversibly* when an infinitesimal change of one of the co-ordinates of the system causes the process to proceed in the opposite direction. Another way of stating this condition is to say that the forces causing the system to change its configuration must be infinitely near equilibrium at every phase of the change. The concept of a *reversible process* is fundamentally important in the theory of Thermodynamics, and the student should note carefully that when we say that a process is reversible we do not mean that it *can* be reversed by some change of conditions, but that it must be reversed by an *infinitesimal* change of an external condition. If the piston moves with friction, a finite change of pressure will be required to reverse its motion, and the process is irreversible.

To sum up, the work done in an isothermal and reversible expansion of 1 mol. of a gas from volume v_1 to volume v_2 is $RT \ln \frac{v_2}{v_1}$. If the process is not reversible, the

work is not given by this expression, but is always less. It varies from zero, as when the gas rushes into a vacuum, to the maximum value $RT\ln\frac{v_2}{v_1}$. This last value is called the *maximum work* of the expansion, since when the process is conducted reversibly, the piston is raising the greatest weight possible.

108. OTHER CASES OF EXPANSION.

(ii) If the expansion is not performed isothermally, the work done is still represented by the integral

$$A = \int_{v_1}^{v_2} p\,dv,$$

but p is now a different function of v.

If the gas is still considered to be ideal

$$p = RT/v,$$

but T is no longer a constant.

If the expansion is performed *adiabatically*, that is, the working substance is expanded or compressed in a cylinder which is a perfect non-conductor of heat, so that no heat is transferred between the working substance and its surroundings, then the law of expansion is

$$pv^\gamma = \text{constant} = c,$$

where $\gamma = c_p/c_v$, the ratio of the specific heats at constant pressure and at constant volume.

$$A = \int_{v_1}^{v_2} p\,dv = c\int_{v_1}^{v_2}\frac{dv}{v^\gamma},$$

$$\therefore A = \frac{c}{1-\gamma}\left(v_2^{1-\gamma} - v_1^{1-\gamma}\right),$$

$$\therefore A = \frac{c}{1-\gamma}\left(\frac{1}{v_2^{\gamma-1}} - \frac{1}{v_1^{\gamma-1}}\right).$$

But $p_1v_1 = RT_1$,

$$p_2v_2 = RT_2,$$

$$\therefore A = \frac{R}{1-\gamma}(T_2 - T_1).$$

The work of adiabatic compression is therefore inde-

pendent of the initial pressure and volume, and the work done by a perfect gas in passing along an adiabatic from one isothermal to another is constant and independent of the path. This work is proportional to the difference of temperature.

(iii) If the gas does not obey Boyle's law,

$$A = \int_{v_1}^{v_2} p\,dv$$

is still true, but instead of

$$pv = \text{const.} \quad (\text{T constant})$$

we must now write

$$p = f(v) \quad (\text{T constant}).$$

The form of the function will depend on the nature of the substance undergoing compression. In the case of strongly compressed gases or liquids, van der Waals has proposed

$$\left(p + \frac{a}{v^2}\right)(v - b) = \text{RT},$$

where a and b are constants.

Clausius gave an equation in which a was regarded as a function of the temperature. Many other equations have been given, but Kammerlingh Onnes concludes that the state of a strongly compressed gas cannot be represented by any equation with a finite number of terms.

Assuming the gas to obey van dar Waals' equation during isothermal expansion :—

$$A = \int_{v_1}^{v_2} p\,dv,$$

where $p = \text{RT}/(v - b) - a/v^2.$

Thence show that

$$A = \text{RT}\ln\frac{v_2 - b}{v_1 - b} - a\left(\frac{1}{v_1} - \frac{1}{v_2}\right).$$

(iv) If the gas obeys van der Waals' equation and expands adiabatically,

$$A = \int_{v_1}^{v_2} p\,dv,$$

where

$$\left(p + \frac{a}{v^2}\right)(v - b)^\gamma = \text{constant} = c,$$

$$\therefore p = \frac{c}{(v - b)^\gamma} - \frac{a}{v^2}.$$

Thence, with the equation

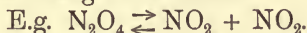$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

show that

$$A = \frac{R}{1 - \gamma}(T_2 - T_1) - a\left(\frac{1}{v_1} - \frac{1}{v_2}\right).$$

### 109. DISSOCIATION.

(v) Let the gas *dissociate* during expansion.

Assume that the original gas, and the products of its dissociation, obey Boyle's law. Two cases arise :—

(a) There is a change of volume.

E.g. $N_2O_4 \rightleftharpoons NO_2 + NO_2$.

In this case the work done on expansion is *greater* than the work which would be obtained from a non-dissociating gas, because the volume increases as new molecules are produced by the dissociation.

(b) There is no change of volume.

E.g. $2HI \rightleftharpoons H_2 + I_2$.
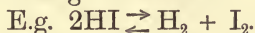
The mixture then behaves exactly like a non-dissociating gas, because for every new molecule produced one of the molecules of the original substance is put out of existence, and the total number of molecules, and therefore the volume, remains constant.

Consider the case of nitrogen peroxide, which has been extensively studied.

$$N_2O_4 \rightleftharpoons NO_2 + NO_2.$$
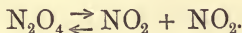
Let n = original number of molecules of N_2O_4 present, x = degree of dissociation, i.e. fraction of molecules dissociated. $(1 - x)n$, $2nx$ are the numbers of molecules of N_2O_4 and NO_2 present at the equilibrium position, and hence, if v = total volume, the law of mass-action gives

$$K \cdot \frac{1 - x}{v} = \frac{x}{v} \cdot \frac{x}{v}$$

$$\therefore Kv = \frac{x^2}{1 - x} \cdot \qquad \qquad (a)$$

The pressures before and after dissociation are proportional to the numbers of molecules present (Avogadro's rule)

$$\therefore \frac{p}{p'} = \frac{n}{(1 - x)n + 2xn} = \frac{1}{1 + x},$$
$$\therefore p' = p(1 + x).$$
$$\text{Now } dA = p'dv = p(1 + x)dv,$$
$$\therefore dA = pdv + xpdv.$$

From Boyle's law and the Mass-law equation (a),

$$p = \frac{c}{v} = \frac{cK(1 - x)}{x^2} \qquad \qquad (b)$$

To find dv we differentiate (a):

$$dv = \frac{2(1 - x)x + x^2}{K(1 - x)^2}dx = \frac{x(2 - x)}{K(1 - x)^2}dx,$$

thence $A = \int_{v_1}^{v_2} pdv + \int_{v_1}^{v_2} xpdv$

$$= c\int_1^{v_2} \frac{dv}{v} + c\int_{x_1}^{x_2}\Big(1 + \frac{1}{1 - x}\Big)dx$$

$$= c\Big(\ln\frac{v_2}{v_1} + x_2 - x_1 - \ln\frac{1 - x_2}{1 - x_1}\Big).$$

But $v_1 = \dfrac{x_1^2}{K(1 - x_1)}$ and similarly v_2; also $c = RT$ from the Horstmann equation,

$$\therefore A = RT\Big\{x_2 - x_1 - 2\ln\frac{x_1(1 - x_2)}{x_2(1 - x_1)}\Big\}.$$

(Examples (i)-(v) are from Nernst-Schönflies.)

(vi) If a solution of an electrolyte is compressed by a semipermeable piston backed by pure solvent, the calculation is exactly similar to that in (v), except that p is now the osmotic pressure, and x the degree of ionisation,

$$x = \Lambda/\Lambda_\infty.$$

Thence, for expansion from volume v_1 to volume v_2,
$$A = RT\left\{\frac{\Lambda_1 - \Lambda_2}{\Lambda_\infty} - 2\ln\frac{\Lambda_1(\Lambda_\infty - \Lambda_2)}{\Lambda_2(\Lambda_\infty - \Lambda_1)}\right\}.$$

110. THE INDICATOR DIAGRAM

The expression $\int pdv$ for the work of a finite expansion is, as we have seen, quite general and independent of the law connecting p and v. So long as the pressure is finite at every point, and varies continuously from point to point, the work of expansion is always equal to the area enclosed by the p-v curve and the x-axis. This area will of course be different for different working substances for the same expansion. The idea of representing an amount of work done on a p-v diagram was first applied by James Watt in studying the efficiency of steam engines. The diagram is called *Watt's Indicator Diagram.*

111. CYCLIC INTEGRALS

Sadi Carnot's fundamental contribution to thermodynamics was the idea of taking the working substance in the cylinder through a *complete cycle* of changes, and so bringing it back to its initial state. Such a cycle is represented on the indicator diagram by a *closed loop*, formed by a curve returning to the initial point.

Let P_1QP_2 represent the *direct process;* P_2RP_1 the *reverse process;* the pair makes up the *cycle,* and is represented by the loop QR.

Let P_1 be (v_1, p_1),

P_2 be (v_2, p_2).

Work done *by* the substance in direct operation
$$= \int pdv = \text{area } P_1QP_2v_2v_1 .$$
Work done *on* the substance in reverse operation
$$= \int pdv = \text{area } P_1RP_2v_2v_1 .$$
$\therefore$ Nett work set free during the cycle
$$= \text{area } P_1QP_2v_2v_1 - \text{area } P_1RP_2v_2v_1$$
$$= \underline{\text{area of loop.}}$$
Thus the work done per cycle = area of loop.

We usually denote this by $(\!\int)\,pdv$, the sign $(\!\int)$ meaning that the integration is taken round the cycle.
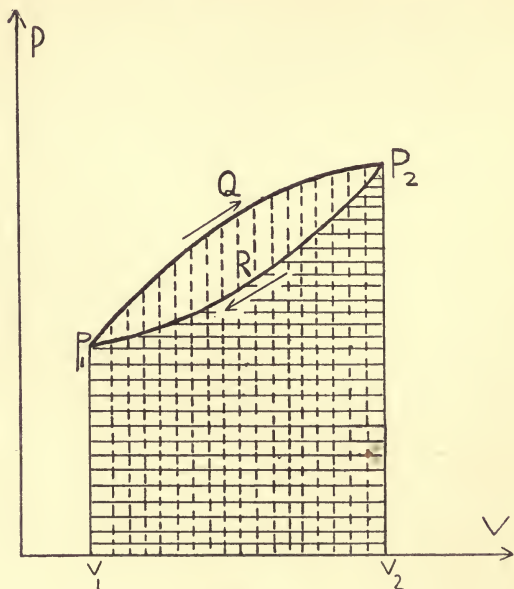

FIG. 36.

112. SIGN OF AN AREA.

We must now consider the sign to be attributed to the area of the loop. If the volume is increasing during the direct process, and decreasing *under lower pressure* in the reverse process, the cyclic loop is traced out *clockwise* and the work done *by* the system is obviously *positive*. But if the reverse process is performed at higher pressure than the direct process, the loop is described *counterclockwise*, and the work done *by* the system is *negative*. If the loop is made up of more than one part, due to intersection of the cyclic curve with itself, each part is treated separately, and the algebraic sum of the areas is the work done.

The diagram illustrates the three cases.

The general method of finding the area of a loop will not concern us, it is described in treatises on the Integral Calculus. Some simple particular cases must, however, be dealt with.

$$\text{If } \phi_1(x) = 0$$

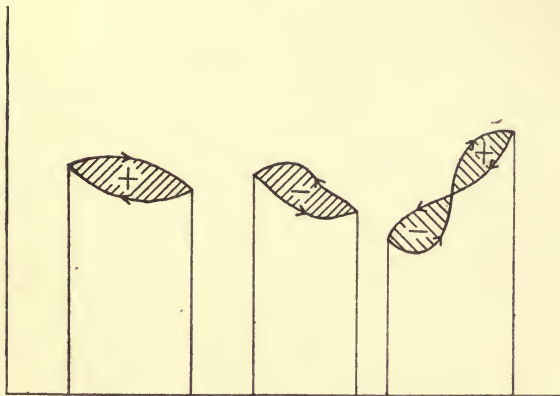be the equation of curve P_1QP_2 in fig. 36, and

$$\phi_2(x) = 0$$

Fig. 37.

that of the curve P_1RP_2, then it is an immediate consequence of our definitions that the area of the loop

$$= \int_{x_1}^{x_2} \phi_1(x)\,dx - \int_{x_1}^{x_2} \phi_2(x)\,dx.$$

113. EXAMPLES

(1) Find the area of the loop enclosed between the two parabolas

$$y^2 = 4x$$
$$x^2 = 4y.$$

These intersect at the origin and (4, 4) as we find by solving for x and y.

$$\text{Area} = \int_0^4 y_1 dx - \int_0^4 y_2 dx$$

$$= \int_0^4 2\sqrt{x}\,dx - \int_0^4 \frac{x^2}{4}dx$$

$$= \left[\frac{x^3}{24} - \frac{2}{3}x^{\frac{3}{2}}\right]_0^4$$

$$= 2\tfrac{2}{3} \text{ sq. cm.}$$

(2) To find the area of the loop in *Carnot's cycle* (*vide* Maxwell, " Theory of Heat "). This consists of four operations performed on a working substance, which we assume to be a perfect gas, contained in an engine cylinder of peculiar construction. The operations are :
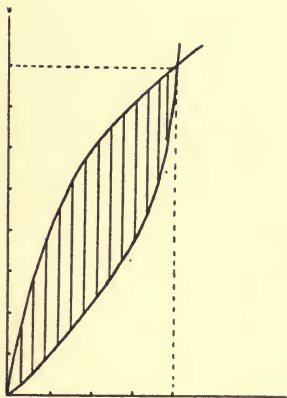

FIG. 38.

(i) Adiabatic compression, from state represented on the *p-v* diagram by A, to that represented by B. (We shall speak of these as " the state A," etc.)

(ii) Isothermal expansion from the state B to the state C.

(iii) Adiabatic expansion from the state C to the state D.

(iv) Isothermal compression from the state D to the initial state A.

Total work = Area of loop ABCD

$$= - \text{A}ab\text{B} + \text{BC}cb + \text{CD}dc - \text{D}da\text{A}.$$

The equations to the various curves are

AB, an *adiabatic* curve, $pv^\gamma = c$ ∴ $p_a v_a{}^\gamma = c_1$, because A lies on AB, p_a, v_a being the pressure and volume at A, and so on.

BC, an *isothermal* curve, $pv = c$ ∴ $p_c v_c = c_2$.

CD, an *adiabatic* curve, $pv^\gamma = c$ ∴ $p_c v_c{}^\gamma = c_3$.

DA, an *isothermal* curve, $pv = c$ ∴ $p_a v_a = c_4$.

But $\text{A}ab\text{B} = \text{CD}dc$,

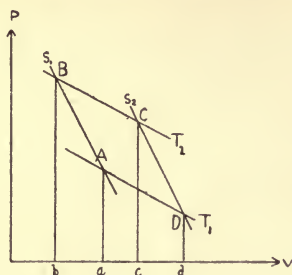since the processes are adiabatic and conducted between

FIG. 39.

the same isothermals, hence these areas, being equal but oppositely signed, cancel; the work is thus equal to

$$BCcb - DdaA$$
$$= c_2 \ln \frac{v_b}{v_c} - c_4 \ln \frac{v_a}{v_d}.$$
$$\text{But } p_b v_b = p_c v_c = c_2,$$
$$p_a v_a{}^\gamma = p_b v_b{}^\gamma = c_1,$$
$$\therefore v_b{}^{\gamma-1} = \frac{c_1}{c_2}.$$
$$\text{Similarly } v_c{}^{\gamma-1} = \frac{c_3}{c_2},$$
$$\therefore \left(\frac{v_b}{v_c}\right)^{\gamma-1} = \frac{c_1}{c_3}.$$
$$\text{Similarly } \left(\frac{v_a}{v_d}\right)^{\gamma-1} = \frac{c_1}{c_3}.$$

Hence

$$c_2 \ln \frac{v_b}{v_c} = \frac{c_2}{\gamma-1} \ln \frac{c_1}{c_3},$$
$$c_4 \ln \frac{v_a}{v_d} = \frac{c_4}{\gamma-1} \ln \frac{c_1}{c_3},$$

$\therefore$ work done per cycle

$$A = \frac{c_2 - c_4}{\gamma-1} \ln \frac{c_3}{c_1}.$$

114. ATTRACTIVE AND REPULSIVE FORCES—THE POTENTIAL FUNCTION

Let the force P exerted between two material particles, electric charges, or magnetic poles, regarded as points, be a function of the distance, x, between the points :—

$$P = f(x) \qquad . \qquad . \qquad . \qquad (1)$$

Consider two point charges of electricity $+ q$ and $+ 1$, separated by a distance x in air, and repelling each other with a force

$$P = q/x^2$$

along the line joining the points.

Let O denote the charge $+ q$, O' the charge $+ 1$, OO' being x.

Let O' be moved towards O by an infinitely small distance $- dx$. The work done by the displacement is

$$dA = - Pdx = - \frac{q}{x^2}dx \qquad . \qquad . \qquad (2)$$

Thus dA is a differential of a function of the distance, of the form $\left(\dfrac{q}{x}\right)$, since

$$d\left(\frac{q}{x}\right) = - \frac{q}{x^2}dx = dA,$$

we define q/x as the *electrical potential, at the point* O', of the quantity of electricity $+ q$, distant x from O'.

For motion of O' over a finite distance x,

$$A = \int_{x_1}^{x_2} \frac{d}{dx}\left(\frac{q}{x}\right)dx = \frac{q}{x_2} - \frac{q}{x_1}.$$

If $x_1 = \infty$, $q/x_1 = 0$, and

$A_{x_2} = q/x_2$ is the potential at a point distant x_2 from O.

Now it is a characteristic property of the potential function that its gradient in any direction is equal to the force in that direction. This follows from the equations

$$P_x = q/x^2,$$
$$A_x = q/x,$$
$$\therefore P_x = - dA_x/dx.$$

$- dA/dx$ therefore measures the tendency of the unit

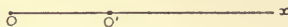charge to leave the vicinity of the charge $+ q$ along the direction Ox.

FIG. 40.

Further, for motion of the charge $+ q$ in an electric field from a point x_1 to a point x_2 in the direction of x, the work done is

$$A = \int_{x_1}^{x_2} (\text{force}) \times dx.$$

But $force = field\ strength \times q,$

and $field\ strength = - dV/dx,$

where V is the electric potential of the field,

$$\therefore A = - q \int_{x_1}^{x_2} \frac{dV}{dx} dx = q(V_{x_1} - V_{x_2}).$$

This work is dependent only on the initial and final positions, and is independent of the path taken by the charge from x_1 to x_2. This characteristic is true generally for potential functions. It may be proved directly by an application of the principle of conservation of energy.

115. THE PERFECT DIFFERENTIAL

We return to the discussion of the equation

$$du = \phi(x, y)dx + \psi(x, y)dy, \qquad (1)$$

where $\phi(x, y)$, $\psi(x, y)$ are functions of the independent variables x and y. Writing this

$$du = Mdx + Ndy, \qquad (1a)$$

we see that two cases arise, according as $\phi(x, y)$ and $\psi(x, y)$, i.e. M and N, do or do not satisfy Euler's criterion :—

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \qquad (2)$$

If condition (2) is satisfied, the expression on the right of (1) or (1a) is immediately integrable; for it is a complete differential of some function of x and y, in which

these are treated as independent variables, formed by the equations :—

$$\frac{\partial}{\partial x}F(x, y) = M \, ;$$

$$\frac{\partial}{\partial y}F(x, y) = N.$$

Thus, by integration, there is obtained at once an equation of the form

$$u = F(x, y) + \text{constant} \qquad . \qquad . \qquad (3)$$

But if (2) is not satisfied, it is not possible to integrate (1), and u cannot be expressed as a function of x and y considered as independent variables. For if

$$u = F(x, y),$$

$$M = \frac{\partial u}{\partial x} = \frac{\partial}{\partial x}F(x, y) \, ;$$

$$N = \frac{\partial u}{dy} = \frac{\partial}{\partial y}F(x, y) \, ;$$

$$\therefore \frac{\partial M}{\partial y} = \frac{\partial^2 F(x, y)}{\partial x \partial y} \, ; \ \frac{\partial N}{\partial x} = \frac{\partial^2 F(x, y)}{\partial y \partial x}.$$

$$\text{But } \frac{\partial^2 F(x, y)}{\partial x \partial y} = \frac{\partial^2 F(x, y)}{\partial y \partial x},$$

$$\therefore \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}, \text{ contrary to the assumption.}$$

If, however, we assume some relation between x and y, so that they are no longer independent variables but one can be expressed as a function of the other, integration again becomes possible. For if

$$f(x, y) = 0 \ . \qquad . \qquad . \qquad (4)$$

i.e. y is an implicit function of x, we can eliminate x or y from (1) and obtain

$$du = \phi(x)dx$$

$$\therefore \ u = F(x) + \text{constant} \qquad . \qquad . \qquad (5)$$

Equations (4) and (5) together may be regarded as forming a solution of (1).

Since $f(x, y)$ may have any form whatever, the number of solutions is infinite.

Geometrically, we may interpret the equations (3), and (4) and (5), as follows :—

Assume that $F(x, y)$ in (3) is a single valued function of the co-ordinates, and that the initial and final positions of the point representing the value of the function in the plane of co-ordinates are known points (x_1, y_1), (x_2, y_2). Then we can find the change in the value of the function u as the point passes from its initial to its final position quite independently of the path.   For

$$u = F(x_2, y_2) - F(x_1, y_1).$$

A potential function, as we have seen, always satisfies this condition.

In the second case, it is quite otherwise.   Of the two equations

$$f(x, y) = 0$$
$$u = F(x) + \text{constant},$$

the first may be regarded as the equation to a curve, and since the form of the second equation depends upon it, the relation between them may be expressed by saying that the change of u during the motion of the point is determinate only when the whole of the path is known, for an infinite number of curves may pass through the initial and final points (x_1, y_1), (x_2, y_2). If the point in its motion describes a *loop*, the initial and final points are identical

$$x_1 = x_2, \, y_1 = y_2,$$

and in the first case (3) $u = 0$, but in the second case u may have any positive or negative value.

This distinction occurs frequently in the study of thermodynamics.   The internal energy ϵ of a system is a function of the first type; this follows at once from the principle of conservation of energy; for if the energy is not completely specified by the co-ordinates defining the state, i.e. is not definite for a given state, then a *perpetuum mobile* would be possible.   Thus if p, v, θ, ϕ are the

14

pressure, volume, temperature, and entropy, we have for a small reversible change

$$d\epsilon = pdv + \theta d\phi \; ;$$

pdv = work absorbed, $\theta d\phi$ = heat absorbed.

This is a perfect differential, by the properties of ϵ,

$$\therefore \; p = \partial\epsilon/\partial v, \; \theta = \partial\epsilon/\partial\phi.$$

Neither pdv nor $\theta d\phi$ are themselves perfect differentials, since the work and heat depend on the path, and a finite quantity of work may be done, or heat absorbed, or both, on passing round a cycle.

116. APPROXIMATE INTEGRATION

If the value of the indefinite integral

$$\int ydx$$

cannot be obtained (either because y cannot be expressed directly in terms of x, or because the function is not integrable), the value of the definite integral $\int_{x_1}^{x_2} ydx$ may often be found, at least approximately. We will consider a few of the common methods :—

(1) *Graphically.*

If y is plotted against x, from the tabulated values, $\int_{x_1}^{x_2} ydx$ is given by the area enclosed between the curve, the ordinates $x = x_1$, $x = x_2$, and the x-axis. This area is found :—

    (*a*) Directly, by counting up the squares.

    (*b*) Indirectly, by cutting out the area, weighing it, and comparing its weight with that of a known area of the same paper.

(2) *By the Planimeter.*

One point of the Amsler planimeter is fixed down, and the other is carried round the boundary of the area. The area is read off directly on the graduated wheels and vernier.

(3) *Trapezoidal Rule.*

Draw n equidistant ordinates of the curve, join their

extremities by straight lines, and so replace the area by the sum of a series of trapeziums. If h = distance between consecutive ordinates, and $y_1, y_2, \ldots y^n$, the lengths of the ordinates, the sum of the trapeziums is

$$\tfrac{1}{2}(y_1 + y_2)h + \tfrac{1}{2}(y_2 + y_3)h + \ldots + \tfrac{1}{2}(y_{n-1} + y_n)h$$
$$= (\tfrac{1}{2}y_1 + y_2 + y_3 + \ldots + y_{n-1} + \tfrac{1}{2}y_n)h.$$

This is only a rough method, giving a result too great or too small according as the curve is convex or concave to the x-axis.

(4) *Newton-Cotes Rule.*

Assume that y is a rational integral function of x of the $(n-1)$th degree:—

$$y = a_0 + a_1x + a_2x^2 + \ldots + a_{n-1}x^{n-1},$$

and determine $a_0, a_1, \ldots$ so that for the n equidistant values of x, y shall have the values $y_1, y_2, y_3. \ldots$ The area is then

$$\int_{x_1}^{x_2} y\,dx = \left[a_0x + \frac{1}{2}a_1x^2 + \frac{1}{3}a_2x^3 + \ldots + \frac{1}{n}a_{n-1}x^n \right]_{x_1}^{x_2}.$$

The coefficients for 3, 4, 5 equidistant ordinates are given below:—

$$\tfrac{1}{3}(y_1 + 4y_2 + y_3)h$$
$$\tfrac{3}{8}(y_1 + 3y_2 + 3y_3 + y_4)h$$
$$\tfrac{2}{45}(7y_1 + 32y_2 + 12y_3 + 32y_4 + 7y_5)h.$$

This is the most exact method.

(5) *Simpson's Rule.*

Let an odd number of ordinates be taken, and the areas between alternate ordinates, beginning with the first, be calculated by the formula $\tfrac{1}{3}(y_1 + 4y_2 + y_3)h$ of the preceding section. If these areas are added, we get the total area, which is therefore given by

$$\tfrac{1}{3}\{y_1 + 4y_2 + y_3 + y_3 + 4y_4 + y_5 + y_5 + 4y_6 + y_7 + \ldots$$
$$+ y_{2n-1} + 4y_n + y_{2n+1}\}h$$
$$= \tfrac{1}{3}\{(y_1 + y_{2n+1}) + 2(y_3 + y_5 + \ldots + y_{2n-1}) + 4(y_2 + y_4$$
$$+ \ldots + y_{2n})\}h.$$

The rule is in words : Take the sum of the first and last ordinates, twice the sum of the other odd ordinates, and four times the sum of the even ordinates. One-

third of the total sum, multiplied by h, gives the required area.

Example :—

Calculate $\log_e 2$ from the formula

$$\log_e 2 = \int_0^1 \frac{dx}{1 + x}.$$

Divide the range into 10 equal intervals, so that $h = 0 \cdot 1$. Calculate values of $y = 1/(1 + x)$ corresponding to values x of 1, $0 \cdot 9$, $0 \cdot 8$, ... 0, and use Simpson's rule. The correct value is $0 \cdot 693147 \ldots$

117. MEAN VALUES OF INTEGRALS

Let $y_1, y_2, y_3 \ldots y_n$ be values of

$$y = f(x)$$

for n equidistant values of x distributed over the range $b - a$. The limiting value to which the arithmetic mean

$$\frac{1}{n}(y_1 + y_2 + y_3 + \ldots + y_n)$$

tends as n is increased indefinitely is called the *mean value* of the function over the range $b - a$.

Now $h = (b - a)/n$ $\therefore$ the above expression

$$= \frac{y_1 h + y_2 h + \ldots + y_n h}{b - a}$$

Also $\underset{h \to 0}{\text{Lim}}$ $(y_1 h + y_2 h + \ldots + y_n h) = \int_a^b f(x) dx,$

$$\therefore \text{mean value} = \frac{1}{b - a} \int_a^b f(x) dx.$$

Geometrically, the mean value is the altitude of a rectangle on the base $(b - a)$ and having an area equal to that under the curve between the ordinates at the extremities of this base. See Fig. 41.

Examples :—

(1) The mean value of the velocity of a falling stone in any interval of *time* t_1 from rest is

$$\frac{1}{t_1} \int_0^{t_1} v\, dt = \frac{1}{t_1} \int_0^{t_1} gt\, dt = \tfrac{1}{2} g t_1,$$

i.e. half the final velocity.

(2) The mean value of the velocity of a falling stone for equal infinitesimal elements of *space s* is, since $v^2 = 2gs$,

$$\frac{1}{s_1}\int_0^{s_1} v\,ds = \frac{\sqrt{2g}}{s_1}\int_0^{s_1}\sqrt{s}\,ds = \frac{2}{3}(2gs_1)^{\frac{1}{2}},$$

i.e. two-thirds the final velocity.

The mean value therefore depends on the choice of the independent variable to which the equal increments are given.
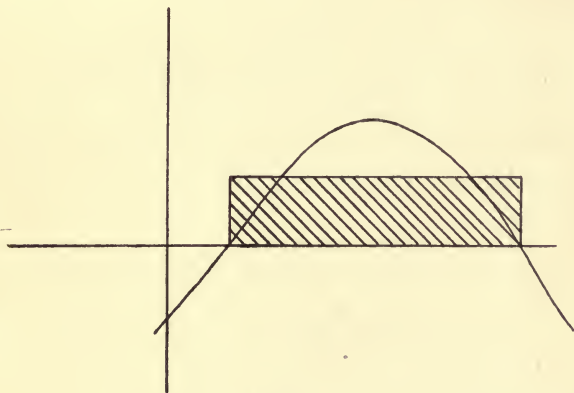
Fɪɢ. 41.

(3) Find the mean value of the velocity of a unimolecular reaction.

(a) For equal intervals of *time*, we have, since

$$x = x_0 e^{-\kappa t},$$
$$v = dx/dt = -\kappa x = -\kappa x_0 e^{-\kappa t},$$
$$\text{mean value} = -\frac{\kappa x_0}{t_1}\int_0^{t_1} e^{-\kappa t}dt = \frac{x_0}{t_1}e^{-\kappa t_1} = \frac{x_1}{t_1}.$$

(b) For equal amounts of *substance* transformed

$$\text{mean value} = \frac{-\kappa}{x_1 - x_0}\int_0^{x_1} x\,dx = \frac{\kappa}{2(x_1 - x_0)}(x_1^2 - x_0^2) = \frac{\kappa}{2}(x_1 + x_0).$$

DIFFERENTIAL EQUATIONS

PART I

118. FORMATION OF A DIFFERENTIAL EQUATION

A RELATION between x, y, and one or more of the derivatives dy/dx, d^2y/dx^2, ... is called a *Differential Equation*.

Examples :—

$$\text{(i) } \frac{dy}{dx} = m.$$

$$\text{(ii) } y = x\frac{dy}{dx}.$$

$$\text{(iii) } \frac{d^2y}{dx^2} - 2m\frac{dy}{dx} + m^2y = 0.$$

If the highest derivative occurring in the equation is the nth derivative, d^ny/dx^n, the equation is of the nth *order*. Thus (i) and (ii) above are of the first order; (iii) is of the second order.

The *degree* of an equation is the highest power of the derivative occurring in it. Thus

$$x\frac{d^2y}{dx^2} - \frac{dy}{dx}$$

is of the second order and the first degree;

$$y\frac{d^2y}{dx^2} + \left(\frac{dy}{dx}\right)^2 = 0$$

is of the second order and second degree.

119. ELIMINATION OF ARBITRARY CONSTANTS

A differential equation may be produced by the process of *Elimination*. If we are given an equation between x, y, and n arbitrary constants, which is called the *Primitive*, then differentiation n times in succession with respect to x will lead to $n + 1$ equations, from which the n constants may be eliminated.

120. EXAMPLES ON ELIMINATION

(1) $y = mx + b$

$$\frac{dy}{dx} = m.$$

b is here an arbitrary constant.

If both constants, m and b, are to be eliminated

$$\frac{d^2y}{dx^2} = 0.$$

(2) $(x - a)^2 + (y - \beta)^2 = a^2$ . . . . (a)

$(x - a) + (y - \beta)\dfrac{dy}{dx} = 0$ . . . . (b)

$1 + \left(\dfrac{dy}{dx}\right)^2 + (y - \beta)\dfrac{d^2y}{dx^2} = 0$ . . . . (c)

Thence

$$a = x + (y - \beta)\frac{dy}{dx} = x - \frac{\left\{1 + \left(\dfrac{dy}{dx}\right)^2\right\}\dfrac{dy}{dx}}{\dfrac{d^2y}{dx^2}}, \text{ and,}$$

$$\beta = y + \frac{\left(\dfrac{dy}{dx}\right)^2 + 1}{\dfrac{d^2y}{dx^2}},$$

from (b) and (c). Substitute in (a)

$$\therefore \left\{\frac{\dfrac{dy}{dx} + \left(\dfrac{dy}{dx}\right)^3}{\dfrac{d^2y}{dx^2}}\right\}^2 + \left\{\frac{\left(\dfrac{dy}{dx}\right)^2 + 1}{\dfrac{d^2y}{dx^2}}\right\}^2 = a^2,$$

$$\text{or } a^2\left(\frac{d^2y}{dx^2}\right)^2 = \left\{1 + \left(\frac{dy}{dx}\right)^2\right\}^3.$$

(3) If $y = ax^2 + bx,$

show that $\dfrac{d^2y}{dx^2} - \dfrac{2}{x} \cdot \dfrac{dy}{dx} + \dfrac{2y}{x^2} = 0.$

(4) If $y = \mathrm{A}e^{ax} + \mathrm{B}e^{\beta x}$ . . . . . (a)

then $\dfrac{dy}{dx} = a\mathrm{A}e^{ax} + \beta\mathrm{B}e^{\beta x}$ . . . . . (b)

and $\dfrac{d^2y}{dx^2} = a^2\mathrm{A}e^{ax} + \beta^2\mathrm{B}e^{\beta x}$ . . . . . (c)

Multiply (a) by $a\beta$ and (b) by β, and subtract :—

$$a\beta y - \beta\frac{dy}{dx} = (a\beta - \beta^2)\mathrm{B}e^{\beta x} \quad . \quad . \quad (d)$$

and, by symmetry,

$$a\beta y - a\frac{dy}{dx} = (a\beta - a^2)\mathrm{A}e^{ax} \quad . \quad . \quad (e)$$

Multiply (b) by a, subtract from (c), and add (d)

$$\therefore \frac{d^2y}{dx^2} - (a + \beta)\frac{dy}{dx} + a\beta y = 0.$$

(5) If $y = \mathrm{A}e^{kx} + \mathrm{B}e^{-kx},$

show that $\dfrac{d^2y}{dx^2} - k^2y = 0.$

(6) If $\phi = \dfrac{\mathrm{A}e^{ka} + \mathrm{B}e^{-ka}}{r},$

show that $\dfrac{d^2\phi}{dr^2} + \dfrac{2}{r} \cdot \dfrac{d\phi}{dr} - k^2\phi = 0.$

121. SOLUTION OF DIFFERENTIAL EQUATIONS

A far more important process than elimination is the inverse process; that is, the recovery of the primitive of a given differential equation. This process is called "solving the differential equation," and will obviously involve one or more integrations, an arbitrary constant appearing with each integration.

122. EXAMPLES

(1) Solve $y \Big/ \dfrac{dy}{dx} = a.$

Whenever possible, we bring all the x's and dx's together, and all the y's and dy's together. This is called

separating the variables. Each side is then integrated, and an arbitrary constant added to one side.

In the example, the variables are separable:—

$$dy/y = dx/a,$$
$$\therefore \log y = x/a + \mathrm{C},$$
$$\therefore y = e^{\frac{x}{a}} \cdot e^{\mathrm{c}}$$
$$\therefore y = be^{\frac{x}{a}},$$
where $b = e^{\mathrm{c}}$.

(2) Solve $dy/dx = -x/y$.
$$x\,dx + y\,dy = 0,$$
$$\therefore x^2 + y^2 = \mathrm{C}.$$

This is the equation of a system of circles with the origin as centre; the radii increase from 0 to ∞ as C is given all positive values from 0 to ∞.

(3) A particle moves in a straight line under an attractive force varying inversely as the square of the distance from a fixed point. Find the velocity at any point.

The equation of motion is

$$v\frac{dv}{dx} = -\frac{\mu}{x^2},$$
$$\therefore v\,dv = -\frac{\mu\,dx}{x^2}$$
$$\therefore \frac{1}{2}v^2 = \frac{\mu}{x} + \mathrm{C}.$$

(4) Abegg states that the dielectric constant of a liquid is related to the temperature by the equation

$$-\frac{dk}{dt} = \frac{k}{190}.$$

Thence show that

$$k = \mathrm{C}e^{-t/190}.$$

(5) Solve $dp/dx = (a - 2p)/x$. $[p = \frac{1}{2}a + \mathrm{C}x^{-2}.]$

(6) Solve $dy/dx = y/(x^2 - 1)$. $\left[y^2 = \mathrm{C}\dfrac{x-1}{x+1}.\right]$

(7) Solve $x^2\dfrac{dy}{dx} + y = 1$. $[y = 1 + \mathrm{C}e^{1/x}.]$

(8) Solve $\dfrac{dy}{dx} + b^2y^2 = a^2$.

Separating the variables :—

$$\frac{dy}{a^2 - b^2y^2} = dx.$$

Split into partial fractions :—

$$\frac{dy}{2a(a - by)} - \frac{dy}{2a(a + by)} = dx.$$

Integrate :—

$$\frac{1}{2ab}\log\frac{a + by}{a - by} = x + C$$

$$\therefore \frac{by + a}{by - a} = Ce^{2abx}.$$

(9) Solve $ax\dfrac{dy}{dx} + 2y = xy\dfrac{dy}{dx}$.

Separate the variables and integrate.

$$x^2y^a = Ce^y.$$

(10) Solve $(1 + y^2)dx - xy(1 + x^2)dy = 0$.
$$[(1 + y^2)(1 + x^2) = Cx^2.]$$

(11) Solve $dy/dx + e^xy = e^xy^2$. $[\log \dfrac{y - 1}{y} = e^x + c.]$

(12) Solve $(xy - x^2)\dfrac{dy}{dx} = y^2$.

We have $xy\dfrac{dy}{dx} = x^2\dfrac{dy}{dx} + y^2$

$\therefore$ dividing through by y and rearranging

$$\frac{x^2}{y}\frac{dy}{dx} = x\frac{dy}{dx} - y,$$

$$\therefore \frac{1}{y}\frac{dy}{dx} = \frac{x\dfrac{dy}{dx} - y}{x^2} = \frac{d}{dx}\Big(\frac{y}{x}\Big).$$

Now integrate, and we get

$$\log y = \frac{y}{x} + C,$$

$$\therefore y = Ce^{\frac{y}{x}}.$$

(13) Solve $y \left/ \dfrac{dy}{dx} \right. = k'x.$　$[y = Cx^k.]$

(14) Solve $y\dfrac{dy}{dx} = kx.$　$[y^2 = kx^2 + c.]$

The student will observe that the integration of the velocity equations in chemical kinetics is really the solution of differential equations with separable variables.

123. HOMOGENEOUS EQUATIONS

An expression is said to be *homogeneous* in respect of two or more variables if each term is of the same dimensions.

$$\text{E.g. } 2x^4y^2 - 3x^3y^3 + x^2y^4 - y^6,$$

is homogeneous and of the sixth degree.

If M, N are homogeneous functions of x and y, of the same degree, the equation

$$M + N\frac{dy}{dx} = 0,$$

is called a *homogeneous differential equation*.

124. EXAMPLES

(i) $x + y \cdot \dfrac{dy}{dx} - 2y = 0.$

Put $y = zx,$
$\therefore dy = xdz + zdx,$
$\therefore$ substituting in the original equation,
$(1 - z)^2dx + xzdz = 0.$

The variables x and z may now be separated :—

$$\frac{dx}{x} + \frac{zdz}{(1 - z)^2} = 0.$$

By integration :—

$$\int\frac{dx}{x} + \int\frac{zdz}{(1 - z)^2} = C,$$
$$\log x + \frac{1}{1 - z} + \log (1 - z) = C.$$

Replacing z by y/x, and simplifying,
$$x/(x - y) + \log (x - y) = C,$$
$$\text{or } (x - y) e^{x/x-y} = C.$$
(ii) $(y - x)dy + ydx = 0.$
Put $x = vy$, and show that
$$y = Ce^{-\frac{x}{y}}.$$
(iii) $(x^2 - y^2)\dfrac{dy}{dx} - 2xy = 0.$

Put $y = vx$, and prove that
$$x^2 + y^2 = Cy.$$

It is obvious from the definition of homogeneous equations that M/N is a function of y/x alone, i.e.
$$\frac{M}{N} = \frac{dy}{dx} = f\left(\frac{y}{x}\right) . \qquad . \qquad . \qquad . \qquad (a)$$

If a straight line $y = mx$, or $\dfrac{y}{x} = m$, be drawn through the origin, the various curves of the system represented by the general solution of (a) have all the same direction at their points of intersection with this line, for then $\dfrac{dy}{dx} = m = $ constant.

Such curves are said to be *similar* and *similarly situated*, the origin being called, in this case, the *centre of similitude*. The curves are those which would be constructed to represent the same equation if we took different units of length. If c is the unit of length, then
$$f\left(\frac{x}{c}, \frac{y}{c}\right) = 0$$
is the general equation of the system, and c is called the *variable parameter*.

(iv) Two liquids, X and Y, are boiling in a still. According to F. D. Brown the ratio of the components passing off as vapour is proportional at every instant to the ratio of the components in the boiling liquid at that instant:
$$\frac{dy}{dx} = a\frac{y}{x}$$
$$\therefore y = Cx^a.$$

(v) $(1 + y^2)dx - xy(1 + x^2)dy = 0$.

We have $\dfrac{dy}{1 + y^2} = \dfrac{dx}{xy(1 + x^2)}$

$\therefore \dfrac{ydy}{1 + y^2} = \dfrac{dx}{x(1 + x^2)}$.

The variables are now separated, and we can integrate by partial fractions:

$$(1 + y^2)(1 + x^2) = Cx^2.$$

(vi) $2xydx + (y^2 - 3x^2)dy = 0$.

Put $y = vx$, and solve as usual.

$$[x^2 - y^2 = Cy^3.]$$

(vii) $(x^2 - 3y^2)xdx + (3x^2 - y^2)ydy = 0$.

$$[(x^2 + y^2)^2 = C(y^2 - x^2).]$$

125. NON-HOMOGENEOUS EQUATIONS

The most general type of such equation is

$$(ax + by + c)dx + (a'x + b'y + c')dy = 0.$$

Assume $x = v + h, y = w + k$,

$\therefore [av + bw + (ah + bk + c)]dv + [a'v + b'w + (a'h + b'k + c')]dw$
$$= 0 \quad . \quad . \quad . \quad (a)$$

Now let h and k be so chosen that

$$ah + bk + c = 0,$$
$$a'h + b'k + c' = 0;$$

i.e. $h = \dfrac{b'c - bc'}{a'b - ab'}, k = \dfrac{ac' - a'c}{a'b - ab'}$. $\quad . \quad (b)$

Substitute in (a), which becomes homogeneous:

$$(av + bw)dv + (a'v + b'w)dw = 0 \quad . \quad (c)$$

126. EXAMPLES

(1) Solve $(3y - 7x - 7)dx + (7y - 3x - 3)dy = 0$.

$$\begin{aligned}
&a = -7 \qquad a' = -3 \\
&b = 3 \qquad\quad b' = 7 \qquad \therefore h = -1 \\
&c = -7 \qquad c' = -3 \qquad k = 0.
\end{aligned}$$

Then $x = v - 1$

$$y = w,$$

and $(-7v + 3w)dv + (-3v + 7w)dw = 0$.

Put $w = vt$ $\therefore$ $dw = vdt + tdv$,
and on substituting and simplifying,

$$7\frac{dv}{v} = -\frac{2dt}{t-1} - \frac{5dt}{t+1}.$$

$\therefore$ $7 \log v + 2 \log (t - 1) + 5 \log (t + 1) = C.$

Replacing $v = x + 1$, $t = w/v = y/(x + 1)$,

$$(y - x - 1)^2(y + x + 1)^5 = C.$$

(2) $(2x + 3y - 5)dy + (2x + 3y - 1)dx = 0.$

In this case $ab' = a'b$, and the above method is no longer applicable, for the denominators of h and k vanish. We put

$$z = ax + by,$$

eliminate y, and obtain

$$a + b\frac{z+c}{mz+c'} + \frac{dz}{dx} = 0,$$

where $a/b = a'/b' = 1/m$. The variables are now separable. The solution is

$$x + y - 4 \log (2x + 3y + 7) = C.$$

127. EXACT EQUATIONS

The equation

$$Mdx + Ndy = 0,$$

where M and N are functions of x and y, is said to be "exact" if M and N satisfy Euler's criterion:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}.$$

(See Part I.)

In this case, the equation has been formed by differentiating a function, u, of x and y, so that

$$u = f(x, y);$$
$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy;$$
$$\text{where } \frac{\partial u}{\partial x} = M, \frac{\partial u}{\partial y} = N.$$

The most general form of function the x-derivative of which is M, is obviously

$$u = \int Mdx + Y;$$

where Y is independent of x, but may be a function of y.

The only other condition is that $\dfrac{du}{dy} = N$,

$$\text{or } N = \frac{d}{dy}\int M dx + \frac{dY}{dy},$$

$$\therefore \frac{dY}{dy} = N - \frac{d}{dy}\int M dx.$$

But Y being a function of y alone, the derivative of the right-hand side with respect to x must vanish, or

$$\frac{dN}{dx} - \frac{dM}{dy} = 0, \text{ as before.}$$

$$\text{Also } Y = \int \frac{dY}{dy} dy = \int \left(N - \frac{d}{dy}\int M dx \right) dy ;$$

$$\therefore u = \int M dx + Y = \int M dx + \int \left(N - \frac{d}{dy}\int M dx \right) dy.$$

This equation enables us to solve any equation which satisfies Euler's criterion. We examine the equation by this criterion first, and if $\partial M/\partial y = \partial N/\partial x$ we can use the above formula.

Examples :—

(1) $x(x + 2y)dx + (x^2 - y^2)dy = 0.$

$$\partial M/\partial y = \partial N/\partial x = 2x,$$

i.e. Euler's criterion is satisfied.

$\int M dx = \int (x^2 + 2xy)dx = \frac{1}{3}x^3 + 2x^2y.$

$$\frac{d}{dy}\int M dx = 2x^2, \; N = x^2 - y^2,$$

$$\therefore N - \frac{d}{dy}\int M dx = x^2 - y^2 - 2x^2 = -y^2 - x^2,$$

$$\therefore \int \left(N - \frac{d}{dy}\int M dx \right) dy = -\int (y^2 + x^2)dy$$
$$= -\frac{1}{3}y^3 - x^2y.$$

Thus, $u = \frac{1}{3}x^3 - \frac{1}{3}y^3 + x^2y,$

is the complete solution of this differential equation.

(2) $(3y^2x - x^2)dy = (2xy - y^3)dx.$

$$[xy^3 = x^2y + C.]$$

(3) $(x^2 - 4xy - 2y^2)dx + (y^2 - 4xy - 2x^2)dy = 0.$

$$[x^3 + y^3 - 6xy(x + y) = C.]$$

128. NON-EXACT EQUATIONS

Equations which do not satisfy Euler's criterion may often be integrated by special devices; for particulars the student is referred to books on differential equations, e.g. Forsyth. We may, however, just mention a few cases which are open to simple treatment.

If the equation

$$M dx + N dy = 0 \qquad . \qquad . \qquad . \qquad (1)$$

is not exact, it implies that some factor has been cancelled out in deriving the equation from the primitive. The equation (1) may be made exact by multiplying it by this factor, called an *integrating factor*, μ. Thus

$$\mu(M dx + N dy) = du = 0 \qquad . \qquad . \qquad (2)$$

Let $x^2 + y^2 = Cy$,

$$\therefore C = y + \frac{x^2}{y}$$

$$\therefore 0 = dy + \frac{2xy dx - x^2 dy}{y^2}$$

$$\therefore 0 = \frac{2xy dx + (y^2 - x^2) dy}{y^2} \qquad . \qquad (i)$$

Now we have previously obtained

$$x^2 + y^2 = Cy$$

by integrating $2xy dx + (y^2 - x^2) dy = 0$ as a homogeneous equation; this is simply the equation (i) with the factor $1/y^2$ cancelled out by multiplying both sides by y^2. Hence $1/y^2$ is the *integrating factor* of

$$2xy dx + (y^2 - x^2) dy = 0;$$

because if we multiply both sides by $1/y^2$ we get

$$\{2xy dx + (y^2 - x^2) dy\} \div y^2 = d\left(y + \frac{x^2}{y}\right) = 0,$$

the solution of which is

$$y + \frac{x^2}{y} = C,$$

$$\text{or } x^2 + y^2 = C.$$

This example also shows that an equation which is not exact, and cannot therefore be solved by the formula

$$u = \int M dx + \int \left(N - \frac{d}{dy} \int M dx \right) dy,$$

can often be solved by another method.

We may also remark that an infinite number of integrating factors exists for $M dx + N dy = 0$, corresponding to various forms of the solution.

E.g. let $y dx - x dy = 0$.

(a) If $\mu = x^{-2}$: $\dfrac{y}{x^2} dx - \dfrac{1}{x} dy = 0$,

$$\therefore \ d\left(\frac{y}{x}\right) = 0,$$

$$\therefore \ y = C'x.$$

(b) If $\mu = x^{-1}y^{-1}$: $\dfrac{dx}{x} - \dfrac{dy}{y} = 0$,

$$\therefore \ \log x - \log y = C,$$

$$\therefore \ \log\frac{x}{y} = C''.$$

(c) If $u = y^{-2}$: $\dfrac{y dx - x dy}{y^2} = 0$,

$$d\left(\frac{x}{y}\right) = 0,$$

$$\therefore \ x = C'''y.$$

It is obvious that all these solutions are equivalent, the constants being related:—

$$C' = 1/C''' = e^{C''}.$$

129. EXAMPLES

(1) $(2x - y + 1)dx + (2y - x - 1)dy = 0.$
$$[x^2 - xy + y^2 + x - y = C.]$$

(2) $x(x^2 + 3y^2)dx + y(y^2 + 3x^2)dy = 0.$
$$[x^4 + 6x^2y^2 + y^4 = C.]$$

(3) $(y - x)dy + y dx = 0.$

This is not exact, since $\partial M/\partial y = 1$, $\partial N/\partial x = -1$.

$$y dx - x dy + y dy = 0.$$

Multiply through by $1/y^2$, and integrate

$$\log y + \frac{x}{y} = C.$$

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(4) $ax^2y^n\dfrac{dy}{dx} = 2x\dfrac{dy}{dx} - y,$

$$\therefore ax^2y^ndy + ydx - 2xdy = 0.$$

Multiply through by y/x^2

$$ay^{n+1}dy + \dfrac{y^2dx - 2xydy}{x^2} = 0.$$

$$d\left(a\dfrac{y^{n+2}}{n+2}\right) + d\left(\dfrac{y^2}{x}\right) = 0,$$

$$\therefore \dfrac{ay^{n+2}}{n+2} + \dfrac{y^2}{x} = \mathrm{C}.$$

(5) $x\dfrac{dy}{dx} - y = x\sqrt{x^2 + y^2}.$

Divide through by x, and put $y = vx$:—

$$v + \dfrac{dv}{dx} - v = x\sqrt{1 + v^2},$$

$$\therefore xdx = \dfrac{dv}{\sqrt{1 + v^2}},$$

$$\therefore \tfrac{1}{2}x^2 = \log\{v + \sqrt{1 + v^2}\} + \mathrm{C},$$

$$\therefore \dfrac{1}{2}x^2 = \log\dfrac{1}{x}\{y + \sqrt{x^2 + y^2}\} + \mathrm{C}.$$

130. LINEAR EQUATIONS

An equation which involves y and its derivatives only in the first degree, is called a "linear" equation. The most general type of linear equation of the first order is *Leibnitz' equation* :

$$\dfrac{dy}{dx} + \mathrm{P}y = \mathrm{Q} \quad . \qquad . \qquad . \qquad (1)$$

where P, Q are either constants, or functions of x.

(i) *P is constant.*

$$\dfrac{dy}{dx} - ay = \mathrm{Q} \quad . \qquad . \qquad . \qquad (2)$$

(a) *If $Q = 0$, the variables are separable,*

$$\dfrac{dy}{y} - adx = 0 \quad . \qquad . \qquad . \qquad (3)$$

$$\therefore \log y - ax = \mathrm{A},$$
$$\text{or } y = \mathrm{C}e^{ax} \quad . \qquad . \qquad . \qquad (4)$$

where $\mathrm{C} = e^{\mathrm{A}}$, is an arbitrary constant.

(b) *If* $Q \neq 0$, we multiply both sides of (3) by e^{-ax}; the left side is now a perfect differential:

$$e^{-ax} \cdot \frac{dy}{dx} - ae^{-ax} = \frac{d}{dx}(e^{-ax}y),$$

$$\therefore \frac{d}{dx}(e^{-ax}y) = Qe^{-ax}. \qquad . \qquad . \qquad (5)$$

Whence $e^{-ax}y = \int Qe^{-ax}dx + C$

or $y = e^{ax}\int Qe^{-ax}dx + Ce^{ax}$ . . . (6)

The solution (6) consists of two parts:

(1) $e^{ax}\int Qe^{-ax}dx$ is called the *particular integral*,

(2) Ce^{-ax} is called the *complementary function*.

One or two special cases may be noticed.

$(a) \qquad\qquad Q = He^{ax}$ . . . . (7)

$\therefore$ multiplying both sides of

$$\frac{dy}{dx} - ay = He^{ax}$$

by the "integrating factor" e^{-ax}, we get

$$\frac{dy}{dx}e^{-ax} - aye^{-ax} = He^{(a-a)x},$$

$$\therefore \frac{d}{dx}(e^{-ax}y) = He^{(a-a)x} \text{ as before,}$$

and $e^{-ax}y = H\int e^{(a-a)x}dx = \frac{H}{a-a}e^{(a-a)x}$,

whence $y = \frac{H}{a-a}e^{x} + Ce^{ax}$ . . . (8)

$(\beta) \qquad$ If $a = a$, or $Q = He^{ax}$ . . . (9)

$\int Qe^{-ax}dx = H\int dx = Hx,$

and $y = Hxe^{ax} + Ce^{ax}$. . . . (10)

$(\gamma) \qquad\qquad Q = Hx^ne^{ax}$ . . . . (11)

$$\int Qe^{-ax} = H\int x^ndx = \frac{Hx^{n+1}}{n+1},$$

$$\therefore y = \frac{Hx^{n+1}}{n+1} + Ce^{ax} \qquad . \qquad . \qquad . \qquad (12)$$

(ii) *P is a function of* x.

$$\frac{dy}{dx} + Py = Q \qquad . \qquad . \qquad . \qquad (1)$$

Let μ be an integrating factor, i.e. a factor which makes

the left-hand side of (1) a perfect differential. Then we may write

$$\mu dy + \mu(Py - Q)dx \equiv Ndy + Mdx,$$

an identity. Thence, by the principle of Undetermined Coefficients,

$$\frac{\partial N}{\partial x} = \frac{\partial \mu}{\partial y}; \; \frac{\partial M}{\partial y} = (Py - Q)\frac{\partial \mu}{\partial y} + P\mu.$$

By Euler's criterion of a perfect differential

$$\frac{\partial N}{\partial x} = \frac{\partial M}{\partial y},$$

$$\therefore \frac{\partial \mu}{\partial x} = (Py - Q)\frac{\partial \mu}{\partial y} + P\mu,$$

$$\therefore \frac{\partial \mu}{\partial x}dx = (Py - Q)\frac{\partial \mu}{\partial y}dx + P\mu dx = -\frac{\partial \mu}{\partial y}dy + P\mu dx,$$

$$\therefore \frac{\partial \mu}{\partial x}dx + \frac{\partial \mu}{\partial y}dy = P\mu dx.$$

But $\frac{\partial \mu}{\partial x}dx + \frac{\partial \mu}{\partial y}dy$ is a perfect differential of a quantity μ, hence

$$d\mu = P\mu dx,$$

$$\therefore P = \frac{1}{\mu} \cdot \frac{d\mu}{dx},$$

$$\therefore \int P dx = \log \mu,$$

$$\therefore (\int P dx) \log e = \log \mu,$$

since $\log e = 1,$

$$\therefore \mu = e^{\int P dx} \qquad . \qquad . \qquad (2)$$

Hence the integrating factor for (1) is $e^{\int P dx}$.

$$e^{\int P dx}(dy + Py dx) = d(y e^{\int P dx}) = e^{\int P dx}Q dx,$$

$$\therefore y e^{\int P dx} = \int e^{\int P dx}Q dx + C,$$

$$\text{or } y = e^{-\int P dx}\int e^{\int P dx}Q dx + Ce^{-\int P dx} \qquad (3)$$

which is an exceedingly important equation.

The student need not remember (3) if he understands the method—"multiply both sides of (1) by $e^{\int P dx}$ and integrate".

131. EXAMPLES ON THE LINEAR EQUATION

(1) Solve $(1 + x^2)\dfrac{dy}{dx} - xy - m = 0$.

Rearrange: $\dfrac{dy}{dx} - \dfrac{x}{1 + x^2}y = \dfrac{m}{1 + x^2}$;

which is now of the form $\dfrac{dy}{dx} + \mathrm{P}y = \mathrm{Q}$.

$\int \mathrm{P}dx = -\int \dfrac{x}{1 + x^2}dx = -\dfrac{1}{2}\log(1 + x^2) = -\log\sqrt{1 + x^2}$.

Integrating factor $= e^{\int \mathrm{P}dx} = e^{-\log\sqrt{1+x^2}} = \dfrac{1}{\sqrt{1 + x^2}}$.

Multiply through by $1/\sqrt{1 + x^2}$ and integrate :
$$y = mx + \mathrm{C}\sqrt{1 + x^2}.$$

(2) Solve $(1 - x^2)dy + (xy - ax)dx = 0$.

[Rearrange as in Example (1), multiply by the integrating factor, and integrate.]
$$y = a + \mathrm{C}\sqrt{1 - x^2}.$$

(3) $\dfrac{dy}{dx} + 2xy = 1 + 2x^2$. $\quad [y = x + \mathrm{C}e^{-x^2}.]$

(4) $xdy + (x + y)dx = 0$. $\quad [x^2 + 2xy = \mathrm{C}.]$

(5) Solve Bernoulli's equation
$$\frac{dy}{dx} + \mathrm{P}y = \mathrm{Q}y^n.$$

Multiply through by $(1 - n)$, and divide through by y^n,

$\therefore \dfrac{1 - n}{y^n} \cdot \dfrac{dy}{dx} + (1 - n)\mathrm{P}y^{1-n} = (1 - n)\mathrm{Q}.$

Put $y^{1-n} = v$

$\therefore \dfrac{dv}{dx} = \dfrac{d(y^{1-n})}{dx} = \dfrac{1 - n}{y^n} \cdot \dfrac{dy}{dx},$

$\therefore \dfrac{dv}{dx} + (1 - n)\mathrm{P}v = (1 - n)\mathrm{Q},$

which is linear in v, the solution being
$$ve^{(1-n)\int \mathrm{P}dx} = (1 - n)\int \mathrm{Q}e^{(1-n)\int \mathrm{P}dx}dx + \mathrm{C}$$
$$\therefore y^{(1-n)} \cdot e^{(1-n)\int \mathrm{P}dx} = (1 - n)\int \mathrm{Q}e^{(1-n)\int \mathrm{P}dx}dx + \mathrm{C}.$$

$$(6) \qquad \frac{dy}{dx} + \frac{y}{x} = y^2.$$

$$\left[\frac{1}{y^2} \cdot \frac{dy}{dx} + \frac{1}{yx} = 1. \right.$$

$$\text{Put } v = 1/y \; \therefore \; \frac{dv}{dx} = -\frac{1}{y^2} \cdot \frac{dy}{dx}.$$

The student will be able to complete the solution

$$Cxy - xy \log x = 1.]$$

$$(7) \qquad \frac{dy}{dx} + n\frac{y}{x} = x^m,$$

$$\therefore x^n \frac{dy}{dx} + nx^{n-1}y = x^{m+n},$$

$$x^n y = \frac{x^{m+n+1}}{m+n+1} + C,$$

$$y = \frac{x^{m+1}}{m+n+1} + Cx^{-n},$$

the integrating factor being obtained on inspection.

(8) The electric current i flowing in a circuit of resistance R and self-induction L is given by Helmholtz' equation

$$L\frac{di}{dt} + iR = E,$$

where E = electromotive force, t = time.

E constant. We have to find the current produced when a constant E. M. F. is acting round the circuit for a time t.

$$\frac{di}{dt} + \frac{Ri}{L} = \frac{E}{L},$$

which is of the standard type. Thence show that

$$i = \frac{E}{R} + Be^{-\frac{Rt}{L}},$$

where B is a constant.

If $i = 0$ when $t = 0$

$$i = \frac{E}{R} - \frac{E}{R}e^{-\frac{Rt}{L}}.$$

The first term is the current according to Ohm's law, the second is the *extra current* at make. As t increases the second term dies away and the current settles down to the steady value E/R. It is a very instructive exer-

cise to plot the value of i against t for given values of E, R, and L (say E = 1 volt, R = 1 ohm, L = 1 henry; i is then given by

$$i = \left(1 - \frac{1}{e^t}\right).)$$

The gradual rise of current after completing the circuit is then clearly seen. The current on breaking the circuit cannot be calculated in this way, on account of the indefinite resistance of the air-gap.

(9) A massive particle subject to a resistance varying as the velocity and to another force which is a given function of the time, obeys the equation of motion

$$\frac{dv}{dt} + kv = f(t).$$

Thence $v = e^{-kt}\int e^{kt} . f(t) . dt + Ce^{-kt}.$

If $f(t) = g$, the acceleration of gravity,

$$v = Ce^{-kt} + g/k.$$

This is the equation for the velocity of a falling raindrop, k being the viscosity of the air. As t increases, v approaches asymptotically a constant value g/k. In this case we have a particle under the influence of forces in equilibrium. The motion of ions in an electrolyte is a similar case.

If $f(t)$ is constant :—

        v increases with time if $f(t) > kv$,

        v decreases with time if $f(t) < kv$.

In both cases $f(t) - kv$ approaches zero asymptotically, and v approaches a limiting value $v_0 = \frac{f(t)}{k}$.

(10) Solve $x dy + y dx = x^3 dx.$ $[\frac{1}{4}x^3 + c/x = y.]$

(11) Solve $\frac{dy}{dt} + k_2 y = k_2 a(1 - e^{-k_1 t}).$

$$\begin{aligned}
y &= Ce^{-\int k_2 dt} + e^{-\int k_2 dt}\int e^{\int k_2 dt} . k_2 a(1 - e^{-k_1 t}) dt \\
&= Ce^{-k_2 t} + e^{-k_2 t}\int e^{k_2 t} . k_2 a(1 - e^{-k_1 t}) dt \\
&= Ce^{-k_2 t} + e^{-k_2 t}\{k_2 a\int e^{k_2 t} dt - k_2 a\int e^{(k_2 - k_1)t} dt\} \\
&= Ce^{-k_2 t} + a - \frac{k_2 a}{k_2 - k_1}e^{-k_1 t}.
\end{aligned}$$

(12) Solve $\dfrac{dy}{dx} + \dfrac{Ky}{a - x} = \dfrac{Kx}{a - x}$.

Integrate as above, then by parts. If $x = 0$ when $y = 0$

$$y = C(a - x)^K + - \frac{K(a - x)}{K - 1},$$

where $C = \dfrac{1}{(K - 1)a^{K-1}}$.

(13) In a chemical reaction let there be present a parts of A, and a parts of C. Let A be changed into a substance B, which then reacts with C.

Let x equivalents of A remain after a time t, and let w equivalents of B remain after the same interval.

The rate of diminution of x is proportional to x :—

$$\frac{dx}{dt} = - k_1 x . \qquad . \qquad . \qquad (1)$$

The rate of diminution of w is proportional to $w \times$ (amount of C present), and the rate of increase of w is equal to the rate of decrease of x :—

$$\frac{dw}{dt} = - k_2 w (x + w) + k_1 x \qquad . \qquad (2)$$

The solution of (1) is

$$x = ae^{-k_1 t} \qquad . \qquad . \qquad . \qquad (3)$$

so that if the residue of x could be measured separately, k_1 could be found. In practice x and w are determined together, and the relation between the total residue $y = x + w$, and the duration of the reaction, t, is very complex.

Adding (1) and (2), we have

$$\frac{dy}{dt} + k_2 wy = 0 \qquad . \qquad . \qquad (4)$$

and if we put $dt = - dx/k_1 x$, from (1) ;

and $w = y - x$, we get

$$\frac{1}{y^2} \frac{dy}{dx} + \frac{k_2}{k_1} \cdot \frac{1}{y} - \frac{k_2}{k_1} \cdot \frac{1}{x} = 0 \qquad . \qquad (5)$$

Put $k_2/k_1 = K$, and we get

$$\frac{1}{y^2} \cdot \frac{dy}{dx} + \frac{K}{y} - \frac{K}{x} = 0 . \qquad . \qquad (5a)$$

Comparing with Bernoulli's equation (Ex. 5)

we put $v = 1/y$, $dv/dx = -\dfrac{1}{y^2} \cdot \dfrac{dy}{dx}$,

$$\therefore \frac{dv}{dx} - Kv - \frac{K}{x} = 0.$$

The integrating factor is e^{-Kx}; also $Q = -K/x$,

$$\therefore ve^{-Kx} = -K\int \frac{1}{x} e^{-Kx} dx + C.$$

The integral cannot be evaluated in finite terms; we have already effected the integration as an infinite series

$$\int \frac{e^{-Kx}}{x} dx = \log x - Kx + \frac{(Kx)^2}{1 \cdot 2^2} - \frac{(Kx)^3}{1 \cdot 2 \cdot 3^2} + \ldots + C,$$

$$\therefore ve^{-Kx} = -K\left\{\log x - Kx + \frac{(Kx)^2}{1 \cdot 2^2} - \frac{(Kx)^3}{1 \cdot 2 \cdot 3^2} + \ldots + C\right\}.$$

Multiply through by ye_{Kx}

$$\therefore 1 = Ke^{Kx}\left\{C - \log x + Kx - \frac{(Kx)^2}{1 \cdot 2^2} + \ldots\right\}y.$$

(14) $\dfrac{dx}{dt} = k(a - x)(x - y)$

where $y = a(1 - e^{-mt})$.

Put $z = 1/K(a - x)$ $\therefore dx = -dz/Kz^2$,

$$\frac{dz}{dt} - Kze^{-mt} = 1,$$

a linear equation of the first order.

Put $P = Ke^{-mt}$ $\therefore e^{\int Pdx} = e^{-\frac{K_e - mt}{m}} = e^{-u}$, say.

Thus $z = Ce^u + \dfrac{e^u}{m}\displaystyle\int \dfrac{e^{-u}}{u} du.$

The latter integral has been treated in Ex. (13).

(15) $\dfrac{dy}{dx} + y = ax^n.$

$[y = a\{x^n - nx^{n-1} + \ldots + (-1)^n n(n-1) \ldots 3 \cdot 2 \cdot 1\} + Ce^{-x}.]$

(16) $dy + \dfrac{n}{(1 + x^2)^{\frac{1}{2}}} y\,dx = \dfrac{a\,dx}{(1 + x^2)^{\frac{1}{2}}}.$

$$\left[\left(y - \frac{a}{n}\right)\{x + (1 + x^2)^{\frac{1}{2}}\}^n = C.\right]$$

Chapter XIII

DIFFERENTIAL EQUATIONS

Part II

132. LINEAR EQUATIONS OF THE SECOND ORDER

THE general linear equation of the second order is

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = R . \qquad . \qquad . \qquad (1)$$

where P, Q, R are functions of x, or constants.

(i) Equations with constant coefficients.

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = 0 . \qquad . \qquad . \qquad (2)$$

is equation (1) minus the right-hand member.

Now the complete solution of (1) may be written

$$y = u + w . \qquad . \qquad . \qquad . \qquad (3)$$

where w is any function whatever which satisfies (1) as it stands, and u is the general solution of (2). For if u is to be determined, and w satisfies (1), we have, by substitution

$$\frac{d^2u}{dx^2} + P\frac{du}{dx} + Qu + \frac{d^2w}{dx^2} + P\frac{dw}{dx} + Qw = R ;$$

but $\frac{d^2w}{dx^2} + P\frac{dw}{dx} + Qw = R$, by hypothesis,

$$\therefore \frac{d^2u}{dx^2} + P\frac{du}{dx} + Qu = 0.$$

i.e. the function u must satisfy (2).

The functions w, u are called the *Particular Integral* and *Complementary Function*, respectively, of the general solution of (1).

The particular integral may be any solution of the

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original equation; it is usual to choose the simplest. The complementary function is the general solution of (2), and involves two arbitrary constants.

If u_1, u_2 are two solutions of (2), then equation (1) is satisfied by

$$y = C_1 u_1 + C_2 u_2,$$

C_1, C_2 being arbitrary constants. This can be verified by substitution. Let the equation be

$$\frac{d^2 y}{dx^2} = -ky.$$

Since u_1, u_2 satisfy this, we have

$$\frac{d^2 u_1}{dx^2} = -ku_1; \quad \frac{d^2 u_2}{dx^2} = -ku_2.$$

Multiplying by C_1, C_2, and adding:—

$$\frac{d^2(C_1 u_1 + C_2 u_2)}{dx^2} = -k(C_1 u_1 + C_2 u_2),$$

which proves the proposition for this case.

This is called the principle of *Superposition of Particular Integrals*.

133. THE OPERATOR D AND THE ALGEBRAIC LAWS

We denote the operating symbol $\frac{d}{dx}$ by D.

Thus $Dy = dy/dx$, $D \log x = 1/x$, etc.

We have already proved that

(i) $D(u + v) = Du + Dv$.

(ii) $(D + a)u = \dfrac{du}{dx} + au = au + \dfrac{du}{dx} = (a + D)u$.

(iii) $D(au) = a\dfrac{du}{dx} = aDu$,

but $D(xy)$ is *not* $= xDy$,

i.e. the commutative law is only obeyed with constant multipliers.

Further, it can be shown that

(iv) $D^m D^n u = D^{m+n} u$.

Thus the operator D, alone, and combined with constant

multipliers, is subject to the algebraic laws.   The following
deductions are immediate :—

(1)   Let $Du = v$,
$$u = D^{-1}v = (1/D)v$$
$$\therefore D^{-1}v = \frac{1}{D}v,$$
or $DD^{-1} = 1$.
Obviously $D^{-1} = \int$.

(2) Let λ_1, λ_2 be any constants, then

$$(D - \lambda_1)(D - \lambda_2)u = (D - \lambda_1)\left(\frac{du}{dx} - \lambda_2 u\right)$$
$$= \frac{d}{dx}\left(\frac{du}{dx} - \lambda_2 u\right) - \lambda_1\left(\frac{du}{dx} - \lambda_2 u\right)$$
$$= \frac{d^2u}{dx^2} - (\lambda_1 + \lambda_2)\frac{du}{dx} + \lambda_1\lambda_2 u$$
$$= [D^2 - (\lambda_1 + \lambda_2)D + \lambda_1\lambda_2]u.$$

This means that any equation of the form

$$\frac{d^2y}{dx^2} - (a + \beta)\frac{dy}{dx} + a\beta y = 0$$

may be written as a product of two factors, since $[D^2 -
(a + \beta)D + a\beta]y$, which is equivalent to that equation,
may be written as

$$(D - a)(D - \beta)y = 0.$$

134. LINEAR EQUATIONS OF THE SECOND ORDER WITH CONSTANT COEFFICIENTS

We return to the consideration of the equation

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = R \ . \qquad . \qquad . \qquad (1)$$

where P, Q, R are, for the present, considered as constants.

We have seen that to solve this we must find two
functions w and u, called the *particular integral*, and the
complementary function respectively, such that

$$y = u + w \ . \qquad . \qquad . \qquad . \qquad (2)$$

Further, w (the particular integral) is any solution
whatever of (1), the simpler the better ; and u (the com-
plementary function) is the most general solution of the
equation

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = 0 . \quad . \quad . \quad (3)$$

and involves two arbitrary constants.

$$\text{Let } P = -(\lambda_1 + \lambda_2),$$
$$Q = \lambda_1\lambda_2 ;$$

then (3) may be written :—

$$D^2y - (\lambda_1 + \lambda_2)Dy + \lambda_1\lambda_2 y = 0,$$
$$\text{or } (D^2 - (\lambda_1 + \lambda_2)D + \lambda_1\lambda_2)y = 0 . \quad . \quad (4)$$

Case (i).

$$P^2 > 4Q ;$$

the roots of (4) are then, by the theory of Quadratic Equations (see appendix), real and unequal

$$(D - \lambda_1)(D - \lambda_2)y = 0 \quad . \quad . \quad (4a),$$

where λ_1, λ_2 are the roots of

$$\lambda^2 + P\lambda + Q = 0 . \quad . \quad . \quad (5)$$

$$\text{i.e. } \left.\begin{matrix}\lambda_1 \\ \lambda_2\end{matrix}\right\} = -\tfrac{1}{2}P \pm \sqrt{\tfrac{1}{4}P^2 - Q}.$$

Equation (5) is called the *auxiliary equation*.

$$\text{Let } (D - \lambda_2)y = z . \quad . \quad . \quad (6)$$

$\therefore$ (4a) becomes

$$(D - \lambda_1)z = 0 . \quad . \quad . \quad (7)$$

which is a linear equation of the first order. The solution of (7) we have shown to be

$$z = Ae^{\lambda_1 x} . \quad . \quad . \quad (8)$$

Substituting in (6), we get

$$(D - \lambda_2)y = Ae^{\lambda_1 x} . \quad . \quad . \quad (9)$$

This is linear, and of the form

$$\frac{dy}{dx} - ay = Q,$$
$$\text{where } Q = He^{ax},$$

discussed in § 130 (*a*) ; and it was shown there that the solution is

$$y = \frac{H}{a - a}e^{ax} + Ce^{ax}.$$

$$\text{Now } a = \lambda_2, a = \lambda_1,$$
$$\therefore y = C_1 e^{\lambda_1 x} + C_2 e^{\lambda_2 x} \quad . \quad . \quad (10)$$

where $C_1 = \dfrac{A}{\lambda_1 - \lambda_2}$; and C_2 is arbitrary.

Since A is arbitrary, both C_1 and C_2 are arbitrary, and (10) is the most general solution of the equation (5).

Case (ii).

If $P^2 = 4Q$, the roots are equal, $\lambda_1 = \lambda_2$.

The equation (9) then becomes

$$(D - \lambda_1)y = Ae^{\lambda_1 x} \qquad . \qquad . \qquad (11)$$

the general solution of which has been found in § 130 (β) to be

$$y = (Ax + B)e^{\lambda_1 x} \qquad . \qquad . \qquad (12)$$

Case (iii).

If $P^2 < 4Q$, the solution involves trigonometric functions, but is never met with in Physical Chemistry.

Summarizing, we may say that the solution of the auxiliary equation

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = 0,$$

when P, Q are constants, takes three forms; according as :

(i) $P^2 > 4Q$;
$$y = C_1 e^{\lambda_1 x} + C_2 e^{\lambda_2 x},$$

where λ_1, λ_2 are the roots of

$$\lambda^2 + P\lambda + Q = 0.$$
(ii) $P^2 = 4Q$;
$$y = (Ax + B)e^{\lambda_1 x}.$$
(iii) $P^2 < 4Q$;

which case does not concern us.

Notice that the above results furnish only the complementary function; if the given equation is of the form

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = 0,$$

they enable us to solve it, but if the form is

$$\frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = R,$$

we have still to find the particular integral.

135. EXAMPLES ON THE LINEAR EQUATION OF THE SECOND ORDER

(1) Solve $x\dfrac{d^2y}{dx^2} = 1$.

We have $\dfrac{d^2y}{dx^2} = 1/x$,

$$\therefore \frac{dy}{dx} = \int\frac{dx}{x} = \log x + C_1.$$

Integrating a second time, we have,

$$y = \int\log x\, dx + \int C_1 dx,$$
$$\therefore y = x \log x - x + C_1 x + C_2,$$
$$\therefore y = x \log x + Ax + B,$$

where $A = C_1 - 1 : B = C_2$.

A similar method enables us to solve

$$\frac{d^2y}{dx^2} = f(x),$$

for $\dfrac{dy}{dx} = \int f(x)\,dx + A$

$$y = \int\{\int f(x)\,dx\}dx + Ax + B,$$

where A, B are arbitrary constants.

(2) Solve $\dfrac{d^2y}{dx^2} = xe^x$.

(Integrate by parts.) $[y = (x - 2)e^x + Ax + B.]$

(3) Solve $x^2\dfrac{d^2y}{dx^2} = a$. $\left[y = a \log \dfrac{a}{x} + Ax + B.\right]$

(4) Solve $\dfrac{d^2y}{dx^2} - 14\dfrac{dy}{dx} - 32y = 0$.

This is written in the symbolic form thus:

$$(D^2 - 14 D - 32)y = 0.$$

The auxiliary equation is

$$\lambda^2 - 14\lambda - 32 = 0,$$
$$\therefore (\lambda - 16)(\lambda + 2) = 0,$$
$$\therefore \lambda_1 = 16, \lambda_2 = -2.$$

The solution of the original equation is therefore

$$y = C_1 e^{16x} + C_2 e^{-2x}.$$

(5) Solve $\dfrac{d^2y}{dx^2} + \dfrac{dy}{dx} = 0$. $[y = A + Be^{-x}.]$

(6) Solve $\dfrac{d^2y}{dx^2} - 3\dfrac{dy}{dx} - 10y = 0.$ $[y = C_1e^{5x} + C_2e^{-2x}.]$

(7) Solve $2\dfrac{d^2y}{dx^2} - 3\dfrac{dy}{dx} + y = 0.$ $[y = C_1e^{x} + C_2e^{\frac{1}{2}x}.]$

(8) Solve $\dfrac{d^3y}{dx^3} - 6\dfrac{d^2y}{dx^2} + 11\dfrac{dy}{dx} - 6y = 0.$

The results proved for equations of the second order may be generalized. The most general type of linear equation with constant coefficients is

$$f(D) . y = 0 ;$$

if $f(D)$ can be resolved into n real factors

$$f(D) = (D - \lambda_1)(D - \lambda_2)(D - \lambda_3) \ldots (D - \lambda_n) ;$$

where $\lambda_1, \lambda_2, \lambda_3 \ldots$ are the (real) roots of

$$f(\lambda) = 0 ;$$

then the solution of

$$f(D)y = 0$$

is the equation

$$y = C_1e^{\lambda_1 x} + C_2e^{\lambda_2 x} + C_3e^{\lambda_3 x} + \ldots + C_ne^{\lambda_n x}$$

involving n arbitrary constants.

$$[y = C_1e^{x} + C_2e^{2x} + C_3e^{3x}.]$$

(9) Solve $\dfrac{d^2y}{dx^2} + 4\dfrac{dy}{dx} + 3y = 0.$

$$[y = C_1e^{3x} + C_2e^{x}.]$$

(10) Solve $\dfrac{d^2y}{dx^2} + 4\dfrac{dy}{dx} + 4 = 0.$

(The auxiliary equation is

$$\lambda^2 + 4\lambda + 4 = 0,$$
$$\therefore (\lambda + 2)^2 = 0,$$

i.e. we have $\lambda_1 = \lambda_2 = -2.$
This is the case of equal roots, hence

$$y = (Ax + B)e^{-2x}.)$$

(11) Solve $\dfrac{d^3y}{dx^3} - \dfrac{d^2y}{dx^2} - \dfrac{dy}{dx} + y = 0.$

(The auxiliary is

$$\lambda^3 - \lambda^2 - \lambda + 1 = 0$$
$$\therefore \lambda_1 = \lambda_2 = 1, \lambda_3 = -1.$$

The case is a combination of equal and unequal roots, and

$$y = (A + Bx)e^x + Ce^{-x}.)$$

(12) Solve $\dfrac{d^3y}{dx^3} - 3\dfrac{d^2y}{dx^2} + 4y = 0.$

$$[y = (A + Bx)e^{2x} + Ce^{-x}.]$$

(13) Solve $\dfrac{d^3y}{dx^3} - 3\dfrac{dy}{dx} + 2y = 0.$

$$[y = (A + Bx)e^x + Ce^{-2x}.]$$

(14) Solve $\dfrac{d^2\theta}{dx^2} - \beta^2\theta = 0.$ $[\theta = C_1 e^{\beta x} + C_2 e^{-\beta x}.]$

(15) Show how to solve an equation of the type

$$\frac{d^2y}{dx^2} = f(y).$$

[The first integral may be obtained in one of two ways :—

(i) Multiply both sides by dy/dx, and integrate

$$\frac{dy}{dx} \cdot \frac{d^2y}{dx^2} = f(y)\frac{dy}{dx}$$

$$\therefore \frac{1}{2}\frac{d}{dx}\left(\frac{dy}{dx}\right)^2 = f(y)\frac{dy}{dx}$$

$$\therefore \frac{1}{2}\left(\frac{dy}{dx}\right)^2 = \int f(y)\frac{dy}{dx}dx + A = \int f(y)dy + A.$$

(ii)   Let $dy/dx = p,$

$$\frac{d^2y}{dx^2} = \frac{dp}{dx} = \frac{dp}{dy} \cdot \frac{dy}{dx} = p\frac{dp}{dy}.$$

Then $\dfrac{d^2y}{dx^2} = f(y)$ may be written

$$p\frac{dp}{dy} = f(y).$$

Integrate with respect to y,

$$\tfrac{1}{2}p^2 = \int f(y)dy + A.$$

In both cases the solution would be completed by separating the variables :—

$$\frac{dy}{\sqrt{2\int f(y)dy + 2A}} = \pm dx.$$

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(16) Solve $\dfrac{d^2y}{dx^2} + y = \dfrac{P}{h^2y^2}$.

$$\left[\left(\dfrac{dy}{dx}\right)^2 + y^2 = 2\int \dfrac{P}{h^2y^2}dy + C.\right]$$

(17) Solve $a\dfrac{d^2y}{dx^2} = \dfrac{dy}{dx}$.

(Put $dy/dx = p$.) $[y = A + Be^{x/a}.]$

(18) Solve $a\dfrac{d^2y}{dx^2} + \left(\dfrac{dy}{dx}\right)^2 = 0$.

$$\text{Put } \dfrac{dy}{dx} = p\,; \ \dfrac{d^2y}{dx^2} = p\dfrac{dp}{dy}$$

$$\therefore a\dfrac{dp}{dy} + p = 0$$

$$\therefore \log p = -\,y/a + C,$$
$$\therefore p = e^{-y/a}e^{C}$$

$$\therefore p = \dfrac{dy}{dx} = Ce^{-y/a}$$

$$\therefore dx/dy = ae^{y/a}$$
$$\therefore x = aae^{y/a} + B,$$
$$\therefore x - B = aae^{y/a},$$
$$\therefore \dfrac{y}{a} = \log \dfrac{x - B}{A}.$$

(19) Solve $\dfrac{d^2V}{dr^2} + \dfrac{1}{r}\dfrac{dV}{dr} = 0$.

In this case the dependent variable (V) does not appear explicitly (cf. Ex. 16.)

$$\text{Put } \dfrac{dV}{dr} = p,$$

$$\therefore \dfrac{dp}{dr} + \dfrac{p}{r} = 0$$

$$\therefore \log p = \log \dfrac{1}{r} + C,$$

$$\therefore p = A/r\,;$$
$$\therefore \dfrac{dV}{dr} = \dfrac{A}{r},\, \therefore dV = A\dfrac{dr}{r},$$

$$\therefore V = A \log r + B.$$

136. LINEAR EQUATIONS WITH VARIABLE COEFFICIENTS

$$\text{Let } \frac{d^2y}{dx^2} + P\frac{dy}{dx} + Qy = 0 \quad . \quad . \quad (1)$$

$$\text{where } P = f_1(x), \ Q = f_2(x).$$

To solve such an equation we put

$$x = e^z \quad . \quad . \quad . \quad . \quad (2)$$

Examples :—

(1) $$x^2\frac{d^2y}{dx^2} + 4x\frac{dy}{dx} + 2y = 0 \quad . \quad . \quad (a)$$

$$\text{Put } x = e^z, \text{ or } z = \log x,$$

$$\therefore \frac{dx}{dz} = e^z, \ e^z\frac{dy}{dx} = \frac{dy}{dz},$$

$$\therefore \frac{dy}{dx} = \frac{1}{x}\frac{dy}{dz} \quad . \quad . \quad . \quad (b)$$

Also

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{1}{x} \cdot \frac{dy}{dz}\right) = \frac{1}{x^2}\left(\frac{d^2y}{dz^2} - \frac{dy}{dz}\right). \quad . \quad (c)$$

Substitute the values from (b) and (c) in (a) :—

$$\frac{d^2y}{dz^2} + z\frac{dy}{dz} + 2y = 0 \ . \quad . \quad . \quad (d)$$

an ordinary linear equation with constant coefficients,

$$\therefore y = C_1e^{2z} + C_2e^z = C_1x^2 + C_2x.$$

(2) Solve $x^2\dfrac{d^3y}{dx^3} + x\dfrac{d^2y}{dx^2} - 4\dfrac{dy}{dx} = 0.$

$$[y = C_1 + C_2/x + C_3x^3.]$$

(3) Solve $(a + x)^2\dfrac{d^2y}{dx^2} - 5(a + x)\dfrac{dy}{dx} + 6y = 0.$

$$\text{Put } z = a + x,$$

$$\therefore z^2\frac{d^2y}{dz^2} - 5z\frac{dy}{dz} + 6y = 0.$$

$$\text{Put } z = a + x = e^t \ \therefore \begin{cases} dx = (a + x)dt \\ d^2x = (a + x)^2dt^2 \end{cases}$$

$$\therefore \frac{d^2y}{dt^2} - 5\frac{dy}{dt} + 6y = 0,$$

$$\therefore y = C_1e^{2t} + C_2e^{3t}, = C_1(a + x)^2 + C_2(a + x)^3.$$

137. CONSECUTIVE CHEMICAL REACTIONS

The view is becoming more and more pronounced that many, perhaps all, the reactions which are represented by complicated equations are in reality composed of a series of simpler reactions, the products of one reaction being involved in the succeeding reactions. These component reactions are usually bimolecular. The frequent occurrence of the bimolecular reaction receives a simple explanation if we accept the molecular theory, since the chance of a binary molecular encounter is very much larger than the chance of a ternary, quaternary, etc., encounter. If one of the component reactions is very much slower than the others, the order of the whole reaction is then approximately that of the slow reaction. Thus if A is converted very slowly into B, and B very quickly into C, the order of the *whole* reaction is practically that of the reaction

$$A \to B;$$

the B, as fast as produced, being converted into C

$$B \to C.$$

Very rapid, or "instantaneous," reactions, such as occur between ions, will have little or no effect on the observed velocity of reaction. Purely hypothetical substances, with this convenient property, may be postulated *ad lib.* in the supposed explanation of a reaction; if no independent evidence of their existence is forthcoming, the "explanation" is simply a complication of the problem to be solved: "It introduces a new unknown; it is unnecessary, and nothing more damning can be said of a scientific theory".

To get a clear idea of the nature of consecutive reactions, we may consider a number of reservoirs on a sloping hill-side connected by pipes of varying diameter. If a quantity of water is let into the first reservoir this will correspond with the initial substance. Since this can only leave the reservoir, its quantity can never tend to a

maximum; on the contrary it will diminish continuously, and approach a minimum value of zero. The rate at which water accumulates in any reservoir will be directly proportional to the head of water in the preceding reservoir and to the cross-section of the inlet pipe; it will be inversely proportional to the cross-section of the outlet pipe. It is evident after a little thought that the quantity of water in such a reservoir can become a maximum after some period of time has elapsed, it then decreases continuously, and approaches asymptotically a minimum value zero. The quantities of water in the reservoirs correspond to the quantities of the products of the component reactions; the cross-sections of the inlet and outlet pipes to the velocity-constants of the reactions in which the product enters and leaves the system. The rate at which any substance Y accumulates is directly proportional to the product of the concentration of the parent substance (X) at any moment and the velocity-constant of the reaction

$$X \to Y.$$

The rate at which the substance Y disappears is proportional to the concentration of Y at any instant multiplied by the velocity-constant of the reaction

$$Y \to Z.$$

Hence the resultant rate of production of Y is given by the equation

$$\frac{dY}{dt} = k_1X - k_2Y.$$

The supply of X is however after a certain point, continually diminishing, and that of Y continuously increasing. The velocity $\frac{dY}{dt}$ will therefore pass through a maximum value, and then diminish. At the maximum point the rates of production of X and Y are in the ratio of $k_2 : k_1$.

Such a system of reactions, in which the various stages are genetically connected, must not be confused with a system of side reactions, in which the original substance

(or substances) are converted *directly* into a variety of final products.

A chemical reaction is the resultant of a large number of conditioning causes. The reaction as a whole must proceed in conformity with the laws of conservation of matter and of energy ; and the available energy of the final system must, if the reaction has occurred spontaneously, be always less than the available energy of the initial system. The actual manner in which the available energy is dissipated will, however, depend largely on the conditions under which the system is placed ; on its temperature and pressure, on the concentrations of the reacting substances, on the extent of the surfaces of the phases, on the opportunity for free diffusion, etc. The reaction therefore proceeds in a variety of ways, and leads to a variety of products. It is only in a few cases that we can say exactly how a reaction proceeds in all its stages.

Instead of taking up the general theory of consecutive reactions, which is still very incomplete, we will consider a few examples which have been actually investigated. We may refer once more to the work of Professors V. Harcourt and W. Esson, of Oxford ; who in their researches "On the Laws of Connexion between the conditions of a chemical change and its amount," " Phil. Trans.," 1866 and 1867, laid the foundations of chemical kinetics. The mathematical and experimental treatment of consecutive reactions was carried out by them in a manner which, when we remember that the general laws of mass-action had not then been enunciated by Guldberg and Waage, can but impress us by its thoroughness and accuracy.
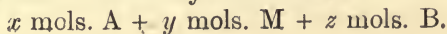
138. CASE 1

Two consecutive unimolecular reactions :—
$$A \to M \to B.$$
M is called the *intermediate product*.
After a time t let the system contain
$$x \text{ mols. A} + y \text{ mols. M} + z \text{ mols. B.}$$

The rates of formation of A, M, B are given by

$$-\frac{dx}{dt} = k_1 x \qquad \qquad (1)$$

$$\frac{dz}{dt} = k_2 y \qquad \qquad (2)$$

$$\frac{dy}{dt} = -\frac{dx}{dt} - \frac{dz}{dt} = k_1 x - k_2 y \qquad (3)$$

Let one mol. of A be the initial amount, then

$$x + y + z = 1 \qquad \qquad (4)$$

Differentiate (2) :—

$$\frac{d^2z}{dt^2} - k_2 \frac{dy}{dt} = 0 \qquad \qquad (5)$$

Add and subtract $k_1 k_2 y$:

$$\frac{d^2z}{dt^2} + (k_1 + k_2)\frac{dz}{dt} - k_1 k_2 (x + y) = 0 \qquad (6)$$

From (4) $z - 1 = -(x + y)$,

$$\therefore \frac{d^2(z-1)}{dt^2} + (k_1 + k_2)\frac{d(z-1)}{dt} + k_1 k_2 (z - 1) = 0 \ . \qquad (7)$$

a linear differential equation of the second order in the variable $(z - 1)$ with constant coefficients.

The solution is therefore

$$z - 1 = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \qquad (8)$$

When $t = 0$, $z = 0$,

$$\therefore -1 = C_1 + C_2 \ . \qquad (9)$$

Differentiate (8) :—

$$dz/dt = -k_1 C_1 e^{-k_1 t} - k_2 C_2 e^{-k_2 t} \qquad (10)$$

From (2), $dz/dt = 0$ when $t = 0$

$$\therefore 0 = -k_1 C_1 - k_2 C_2 \ . \qquad (11)$$

From (9) and (11)

$$C_1 = \frac{k_2}{k_1 - k_2}; \ C_2 = -\frac{k_1}{k_1 - k_2},$$

$$\therefore z - 1 = \frac{k_1}{k_1 - k_2} e^{-k_2 t} - \frac{k_2}{k_1 - k_2} e^{-k_1 t} \ . \qquad (12)$$

Put $k_2/(k_1 - k_2) = A$; $k_1/(k_1 - k_2) = B$;

$$e^{-k_1} = C ; \ e^{-k_2} = D \ . \qquad (13)$$

Then $x + y = B(C)^t - A(D)^t$. , . (14)

Values of A, B, C, D may be calculated which satisfy the data. Harcourt and Esson found an example of this case in the reduction of $KMnO_4$ by oxalic acid. Manganese dioxide is first formed by an instantaneous reaction, and is then slowly reduced to MnO *via* an intermediate oxide, possibly Mn_4O_7 :—

$$MnO_2 \rightarrow Mn_4O_7 \rightarrow MnO.$$
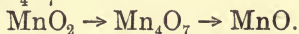
They found that A = 28·5, B = 0·82, C = 2·7, D = 0·98, satisfied the data.

Calculate the values of $(x + y)$ for t = 0·5, 1·0, 1·5, ... 4·0, and compare with the following experimental numbers :—

t =	0·5	1·0	1·5	2·0	2·5	3·0	3·5	4·0
$x + y$ =	25·85	21·55	17·90	14·90	12·55	10·45	8·95	7·70

139. CASE 2. MONOMOLECULAR FOLLOWED BY BIMOLECULAR REACTION

If $KMnO_4$, $MnSO_4$, $C_2H_2O_4$, and H_2SO_4 are mixed in the proportions :—

$$2KMnO_4 + 15MnSO_4 + 5C_2H_2O_4 + 3H_2SO_4,$$

(instead of $2KMnO_4 + 14MnSO_4 + 108C_2H_2O_4 + 760H_2SO_4$ as in case (1)) the following reactions appear to take place:

(i) $2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4,$
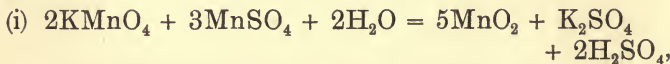
or, since everything except $KMnO_4$ is in excess,

$$KMnO_4 \rightarrow MnO_2.$$
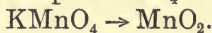
If x = concentration of $KMnO_4$ after a time t,

$$-\frac{dx}{dt} = k_1 x . \qquad . \qquad . \qquad . \qquad (1)$$

(ii) Reduction of the MnO_2 formed in (i) by the oxalic acid now takes place :—

$$MnO_2 + C_2H_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2,$$
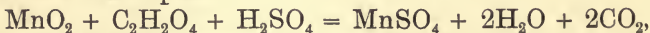
or since H_2SO_4 is present in excess :—

$$MnO_2 + C_2H_2O_4 \rightarrow MnO + 2H_2O + 2CO_2.$$

Let y, z = concentrations of MnO_2 and $C_2H_2O_4$ in the solution after a time t,

$$- \frac{dz}{dt} = k_2 yz \quad . \qquad . \qquad . \qquad (2)$$

$$\text{Also } \frac{dy}{dt} = k_1 x - k_2 yz . \qquad . \qquad . \qquad (3)$$

If the amounts of $KMnO_4$ and MnO_2 are determined together, and if a is the amount of $C_2H_2O_4$ or $KMnO_4$ originally present (in gram equivalents),

$a - x$ = number of equivalents of $KMnO_4$ transformed at time t.

$a - z$ = number of equivalents of $C_2H_2O_4$ transformed at time t.

But (number of equivalents of $KMnO_4$ transformed) = (number of equivalents of MnO_2 transformed) + (number of equivalents free MnO_2), from the equations,

$$\therefore a - x = a - z + y \therefore z = x + y \qquad . \qquad (4)$$

Divide (3) by (1),

$$- \frac{dy}{dt} \cdot \frac{dt}{dx} = 1 - \frac{k_1}{k_2} \cdot \frac{yz}{x}.$$

Substitute $dy = dz - dx$, from (4), and put $k_1/k_2 = K$:—

$$- \frac{dz}{dx} = - K\frac{yz}{x}.$$

Substitute $y = (z - x)$, and divide through by z^2 :—

$$\frac{1}{z^2} \cdot \frac{dz}{dx} + \frac{K}{z} - \frac{K}{x} = 0 \quad . \qquad . \qquad . \qquad (5)$$

This has been solved in Example (13) on § 131 :—

$$Ke^{-Kx}\left\{C_1 - \log x + Kx - \frac{1}{1.2^2}(Kx)^2 + \dots\right\}z = 1 \quad . \qquad (6)$$

Integrating (1) :—

$$\int\frac{dx}{x} = - \int k_1 dt + \text{const.}$$

$$\therefore \log x = - k_1 t + \text{const.,}$$

$$\text{or } x = ae^{-k_1 t} \qquad . \qquad . \qquad . \qquad (7)$$

Substitute this value of x in (b) and neglect the terms after $\log x$ (after five minutes, it was found that the permanganate had practically disappeared) :—

$$\frac{k_2}{k_1}(C_1 - \log a + k_1 t)z = 1,$$

or, collecting the constants,

$$(C + t)z = 1/k_2 \qquad . \qquad . \qquad . \qquad (8)$$

The values $C = 0.1$, $k_2 = 0.006364$ were found to give good results when compared with experiment.

140. RADIOACTIVE CHANGES

The emanations of radium and thorium; and the substances "uranium X" and "thorium X," produced in the disintegration of uranium and thorium, lose their activity according to the simple exponential law previously considered. The change is monomolecular, involves the disintegration of a single atom, and proceeds according to the equation

$$x = x_0 e^{-\lambda t}.$$

The "excited radioactivity" produced on a body (e.g. a platinum plate) exposed to the emanations of thorium, radium, and actinium, does not decay in such a simple manner; Rutherford therefore suggests that the deposited matter undergoes a series of successive changes, the process being an example of consecutive reactions. It was found that the rate of decay was quite different according as the body had been exposed for a short time or for a long time to the action of the emanation. We shall therefore have to consider the phenomena in the cases of "short exposure" and "long exposure".

We will take the first part of the life of radium. This is composed of the following stages :—

$$\text{Ra} \to \text{Ra Examination} \to \underbrace{\text{RaA} \to \text{RaB} \to \text{RaC}}_{\text{active deposit}} \to$$
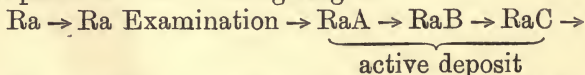
Each change, involving the disintegration of a single atom, is unimolecular, and if N, N_0 are the number of atoms of any changing substance present at time t, and the number of atoms present when it begins to disintegrate, respectively,

$$N = N_0 e^{-\lambda t};$$

where λ is the *radioactive constant*.

This is the integral form of the velocity equation

$$\frac{dN}{dt} = - \lambda N.$$

(a) Let N_1, N_2, N_3, be the numbers of atoms of RaA, RaB, RaC left unchanged after a time t. Let λ_1, λ_2, λ_3 be the radioactive constants for the same three substances; and, in the case of a short exposure, we may consider, say, N atoms of A deposited, these changing into B and C.
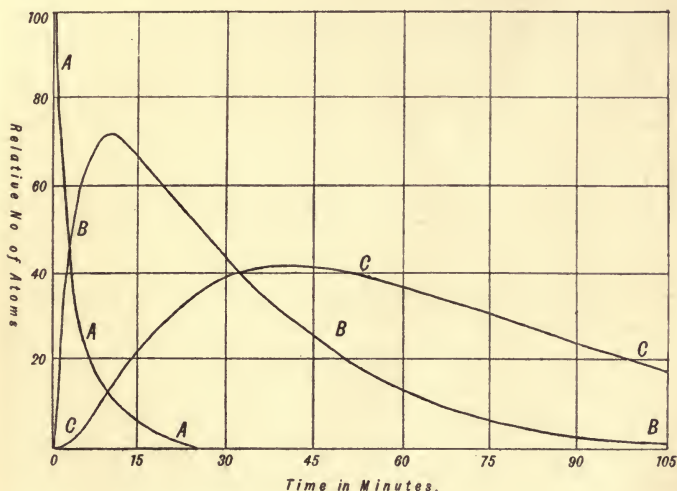
FIG. 42.

$$N_1 = N e^{-\lambda_1 t} \qquad \qquad (1)$$

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2 \qquad \qquad (2)$$

$$\frac{dN_3}{dt} = \lambda_2 N_2 - \lambda_3 N_3 \qquad \qquad (3)$$

Therefore $\dfrac{dN_2}{dt} = \lambda_1 N e^{-\lambda_1 t} - \lambda_2 N_2 \qquad (4)$

the solution of this being of the form

$$N_2 = N(a e^{-\lambda_1 t} + b e^{-\lambda_2 t}) \qquad (5)$$

where $a = \lambda_1/(\lambda_2 - \lambda_1)$.

Since $N_2 = 0$ when $t = 0$ $\therefore b = -\lambda_1(\lambda_2 - \lambda_1)$.

$$\therefore N_2 = \frac{N\lambda_1}{\lambda_1 - \lambda_2}(e^{-\lambda_2 t} - e^{-\lambda_1 t}) \qquad . \qquad . \qquad . \qquad (6)$$

Substituting in (3) it is found that

$$N_3 = N(ae^{-\lambda_1 t} + be^{-\lambda_2 t} + ce^{-\lambda_3 t}) \qquad . \qquad . \qquad (7)$$

where $a = \dfrac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)}$; $b = \dfrac{-\lambda_1 \lambda_2}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)}$;

$c = \dfrac{\lambda_1 \lambda_2}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}$.

FIG. 43.

If the curves showing the amounts of A, B, C present at any time t after a short exposure be drawn from (1), (5), (7), the variation of the three substances is evident. In the case of radium,

$$\lambda_1 = 3 \cdot 85 \times 10^{-3},$$
$$\lambda_2 = 5 \cdot 38 \times 10^{-4},$$
$$\lambda_3 = 4 \cdot 13 \times 10^{-4}.$$

If $N = 100$, and the amounts of B and C be taken as initially zero, the curves for the production of B and C,

and the decay of A may be drawn.   These are given in Fig. 42.

(b) In the case of a *long exposure*, the emanation and its products have reached a state of equilibrium, in which the number of atoms of A deposited per second from the emanation, change into the same number of atoms of B, and so on.   Let n_0 be this number.

$$n_0 = \lambda_1 N_1^0 = \lambda_2 N_2^0 = \lambda_3 N_3^0 \quad . \quad . \quad (1)$$

where N_1^0, etc. are the values for the steady state.

Initially, $N_1 = N_1^0 = n_0/\lambda_1,$
$$N_2 = N_2^0 = n_0/\lambda_2,$$
$$N_3 = N_3^0 = n_0/\lambda_3 \quad . \quad . \quad (2)$$

hence, as before

$$N_1 = \frac{n_0}{\lambda_1} e^{-\lambda_1 t} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$N_2 = \frac{n_0}{\lambda_1 - \lambda_2}\left(\frac{\lambda_1}{\lambda_2} e^{-\lambda_2 t} - e^{-\lambda_1 t}\right) \quad . \quad . \quad (4)$$

$$N_3 = n_0(a e^{-\lambda_1 t} + b e^{-\lambda_2 t} + c e^{-\lambda_3 t}) \quad . \quad (5)$$

where $a = \dfrac{\lambda_2}{(\lambda_1 - \lambda_2)(\lambda_1 - \lambda_3)}$, $b = \dfrac{-\lambda_1}{(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)}$,

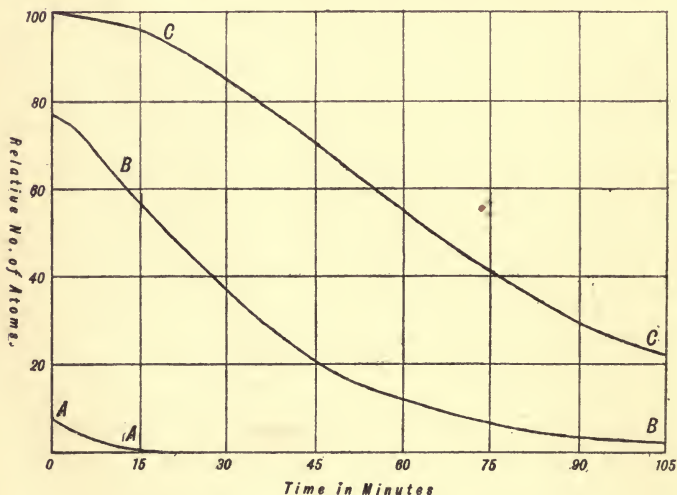$c = \dfrac{\lambda_1 \lambda_2}{\lambda_3(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)}.$

Taking the value $N_3^0 = 100$, and the values of $\lambda_1, \lambda_2, \lambda_3$ already given, the curves for the change of the active deposit after long exposure may be drawn.   They are given in Fig. 43.

Appendix I

THE THEORY OF QUADRATIC EQUATIONS

THE general type of quadratic equation is
$$ax^2 + bx + c = 0 \qquad . \qquad . \qquad (1)$$
where a, b, c are constants. In proceeding to the solution of this equation, we observe in the first place that
$$(x + a)^2 = x^2 + 2ax + a^2,$$
in which both members are complete squares.

Any quadratic expression is a complete square when the third term is the square of half the coefficient of x, provided the coefficient of x^2 is unity.

Divide (1) by a, and transpose :—
$$x^2 + \frac{b}{a}x = -\frac{c}{a}.$$

Complete the square of the expression on the left by adding $\left(\frac{b}{2a}\right)^2$ to both sides :—

$$x^2 + \frac{b}{a}x + \left(\frac{b}{2a}\right)^2 = -\frac{c}{a} + \frac{b^2}{4a^2},$$
$$\therefore \left(x + \frac{b}{2a}\right)^2 = \frac{b^2 - 4ac}{4a^2},$$
$$\therefore x + \frac{b}{2a} = \pm \frac{\sqrt{b^2 - 4ac}}{2a},$$
$$\therefore x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad . \qquad (2)$$

We observe that every quadratic equation has two *roots*, i.e. two values of x which satisfy the equation. These roots are

$$x_1 = \frac{-b + \sqrt{b^2 - 4ac}}{2a}, \quad x_2, \frac{-b - \sqrt{b^2 - 4ac}}{2a}.$$

If we denote the roots by a and β, we have

$$a + \beta = \frac{-b + \sqrt{b^2 - 4ac}}{2a} + \frac{-b - \sqrt{b^2 - 4ac}}{2a} = -\frac{b}{a},$$

or the *sum of the roots* $= -\dfrac{\text{coefficient of } x}{\text{coefficient of } x^2}$.

Also

$$a\beta = \left(-\frac{b}{2a} + \frac{\sqrt{b^2 - 4ac}}{2a}\right)\left(-\frac{b}{2a} - \frac{\sqrt{b^2 - 4ac}}{2a}\right)$$

$$= \frac{b^2}{4a^2} - \frac{b^2 - 4ac}{4a^2} = \frac{c}{a},$$

or the *product of the roots* $= \dfrac{\text{third term}}{\text{coefficient of } x^2}$.

Examples :—

(1) Show that the sum of the roots of
$ax^2 - ax + c = 0$ is unity.

(2) Show that the product of the roots of
$acx^2 + b^2x + c^2 = 0$
is that of the roots of
$ax^2 + bx + c = 0$.

(3) Let a, β be the roots of
$ax^2 + bx + c = 0$.

Show that the factors of this expression are
$a(x - a)(x - \beta) = 0$.

This result enables us to factorize any quadratic expression very readily.

Consider the equation

$$ax^2 + bx + c = 0,$$

where a, b, c are real quantities, i.e. do not involve the square root of a negative quantity.

The roots we have shown to be

$$a = \frac{-b + \sqrt{b^2 - 4ac}}{2a}; \quad \beta = \frac{-b - \sqrt{b^2 - 4ac}}{2a}.$$

Now all questions as to the nature of the roots may be answered, without actually solving the equation, from a

consideration of the expression $(b^2 - 4ac)$. This expression is therefore called the *discriminant* of the equation.

(i) If $b^2 - 4ac$ is *negative*, i.e. if $b^2 < 4ac$, the roots are *imaginary*, since the square root of a negative quantity is not a real quantity.

(ii) If $b^2 - 4ac$ is *zero*, i.e. if $b^2 = 4ac$, the roots are *real* and *equal*.

(iii) If $b^2 - 4ac$ is *positive*, i.e. if $b^2 > 4ac$, the roots are *real* and *unequal*.

(iv) If $b^2 - 4ac$ is a *perfect square*, the roots are *rational*.

(The distinction between " real " quantities and " rational " quantities must be kept clear. $\sqrt{2}$ is real but irrational, $\sqrt{-2}$ is unreal, or imaginary.)

(v) If $b^2 - 4ac$ is *not a perfect square*, the roots are irrational.

Formation of Quadratic Equations :—

Given the roots m and n, it is required to form the quadratic equation.

Let the coefficient of $x^2 = 1$, then

$$\text{coefficient of } x = -(m + n),$$
$$\text{third term} = mn,$$

∴ the equation required is

$$x^2 - (m + n)x + mn = 0.$$

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Appendix II

THE SOLUTION OF SYSTEMS OF LINEAR EQUATIONS BY DETERMINANTS

Systems of equations of the types

$$\left.\begin{array}{l} a_1x + b_1y = c_1 \\ a_2x + b_2y = c_2 \end{array}\right\} \qquad . \qquad . \qquad \text{(A)}$$

$$\left.\begin{array}{l} a_1x + b_1y + c_1z = d_1 \\ a_2x + b_2y + c_2z = d_2 \\ a_3x + b_3y + c_3z = d_3 \end{array}\right\} \qquad . \qquad . \qquad \text{(B)}$$

occur frequently in practical work.

Now it is shown in textbooks on Algebra that the solution of (A) may be written

$$x = \frac{\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}}; \quad y = \frac{\begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}} \qquad . \qquad . \qquad \text{(A')}$$

where $\begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix} = a_1c_2 - a_2c_1$,

i.e. we take cross products; descending products being positive, ascending products negative.

Similarly $\begin{vmatrix} b_1 c_1 \\ b_2 c_2 \end{vmatrix} = b_1c_2 - b_2c_1$, etc.

The symbol $\begin{vmatrix} a_1 c_1 \\ a_2 c_2 \end{vmatrix}$ is called a *Determinant*; the pro-

cess of writing out the products, in conformity with the rule, is called *expanding* the determinant. The utility of determinants lies in the compactness and symmetry which they introduce into algebraical operations.

All simultaneous equations of type (A) may be solved by introducing proper values of the constants into (A').

If the equations involve three unknowns, x, y, and z, simultaneously, the determinant equations are

$$x = \frac{\begin{vmatrix} d_1 & b_1 & c_1 \\ d_2 & b_2 & c_2 \\ d_3 & b_3 & c_3 \end{vmatrix}}{\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}} = \frac{\mathrm{D}(d,b,c)}{\mathrm{D}(a,b,c)} \text{ say,}$$

$$y = \frac{\mathrm{D}(a,d,c)}{\mathrm{D}(a,b,c)},$$

$$z = \frac{\mathrm{D}(a,b,d)}{\mathrm{D}(a,b,c)}.$$

The determinants in these equations are expanded by the following rule :—

Rule of Sarrus : repeat the first two columns after the third column, make products along the diagonals as shown, counting descending $^{+}$", ascending $^{-}$".

$$= a_1 b_2 c_3 + b_1 c_2 a_3 + c_1 a_2 b_3 - a_3 b_2 c_1 - b_3 c_2 a_1 - c_3 a_2 b_1.$$

Another method is to expand the determinant into its *minors* :—

$$\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} = a_1 \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} - a_2 \begin{vmatrix} b_1 & c_1 \\ b_3 & c_3 \end{vmatrix} + a_3 \begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix}.$$

Then, expanding the minor determinants, we get

$$a_1(b_2c_3 - b_3c_2) - a_2(b_1c_3 - b_3c_1) + a_3(b_1c_2 - b_2c_1).$$

Further particulars respecting Determinants must be looked for in textbooks on Algebra.

Examples :—

(1) Solve the equations

$$2x + 3y + z = 20$$
$$3x + 5y + 7z = 34$$
$$x + 2y + 4z = 17.$$
$$(x = 1, \; y = 2, \; z = 3.)$$

(2) *Field* estimated the chlorine, bromine, and iodine in a mixture of a chloride, a bromide, and an iodide, by precipitating one-third with silver nitrate and weighing the mixed halides, precipitating another third with silver nitrate and digesting the precipitate with KBr, when $AgCl \rightarrow AgBr$, since the solubility-product of the latter is less; and finally by digesting the precipitate from the remaining third with KI, when $AgCl \rightarrow AgI$, $AgBr \rightarrow AgI$.

Let w, w', w'' be the weights of the three precipitates after treatment; x, y, z the (unknown) amounts of AgCl, AgBr, AgI. The student will easily prove that

$$x + y + z = w$$
$$\frac{186\cdot49}{142\cdot32}x + y + z = w'$$
$$\frac{233\cdot04}{142\cdot32}x + \frac{233\cdot04}{186\cdot49}y + z = w''.$$

Thence find x, y, z by determinants.

(3) *Macnair* treated the mixture of AgCl, AgBr and AgI with $K_2Cr_2O_7 + H_2SO_4$, thus converting AgCl and AgBr into soluble Ag_2SO_4, and AgI into insoluble $AgIO_3$. The iodate was reduced to Ag, and the Ag in the filtrate estimated. Let w = weight of mixed halides; w_1 = weight of Ag from $AgIO_3$; w_2 = weight of Ag from AgCl and AgBr.

Prove that

$$x + y + z = w$$
$$z = \frac{\text{AgI}}{\text{Ag}}w_1$$
$$x\frac{\text{Ag}}{\text{AgCl}} + y\frac{\text{Ag}}{\text{AgBr}} = w_2.$$

Thence find x, y, z by determinants.

(4) Sodium and potassium may be estimated by the evaporation of a mixture of their salts (with a volatile acid) with strong hydrochloric acid. $\text{NaCl}(x)$ and $\text{KCl}(y)$ remain. Let the weight of the residue be w_1:

$$x + y = w_1.$$

The mixture is evaporated with strong sulphuric acid and the residual sulphates weigh, say, w_2:

$$\frac{71}{57 \cdot 5}x + \frac{87}{74 \cdot 5}y = w_2.$$

Thence find x and y by determinants.

(See Ostwald, "Principles of Inorganic Chemistry," trans. A. Findlay, 1902, p. 472).

(5) A mixture of x vols. ethylene, y vols. proplyene, and z vols. benzene vapour is measured in the gas burette. Its volume $= a$. It is then mixed with excess of oxygen and fired. The contraction $= b$. The residual gas is passed into the potash pipette and back to the burette. The contraction $= c$. From the equations prove that

$$x + y + z = a$$
$$2x + \tfrac{5}{2}y + \tfrac{5}{2}z = b$$
$$2x + 3y + 6z = c.$$

Thence find x, y, z by determinants.

Appendix III

APPROXIMATION FORMULÆ

If the magnitudes a, b, c, d are small in comparison with unity, it is true to a first approximation that:

(1) $(1 \pm a)(1 \pm b)(1 \pm c) \ldots = 1 \pm a \pm b \pm c \pm \ldots$

(2) $\qquad (1 \pm a)^2 = 1 \pm 2a.$

(3) $\qquad (1 \pm a)^3 = 1 \pm 3a.$

(4) $\qquad (1 \pm a)^n = 1 \pm na.$

(5) $\qquad \sqrt{(1 \pm a)} = 1 \pm \tfrac{1}{2}a.$

(6) $\qquad \sqrt[3]{1 \pm a} = 1 \pm \tfrac{1}{3}a.$

(7) $\qquad \sqrt{ab} = \tfrac{1}{2}(a + b).$

(The first member is the so-called *geometric mean*, the second is the *arithmetic mean*.)

(8) $\qquad \dfrac{1}{1 \pm a} = 1 \mp a.$

(9) $\qquad \dfrac{1}{(1 \pm a)^{\frac{1}{2}}} = 1 \mp \tfrac{1}{2}a.$

(10) $\qquad \dfrac{1}{(1 \pm a)^n} = 1 \mp na.$

(11) $\qquad \dfrac{(1 \pm a)(1 \pm b)}{(1 \pm c)(1 \pm d)} = 1 \pm a \pm b \mp c \mp d.$

(12) $\qquad e^a = 1 + a.$

(13) $\qquad x^a = 1 + a \log x.$

(14) $\qquad \log_e(1 + a) = a^e - \dfrac{a^2}{2}.$

The student should verify the above formulæ. Further examples (mainly modifications of the types just given) are added.

Examples :—

Show that to the first order of approximation, if δ is small compared with a :

$$(1) \qquad \frac{1}{a + \delta} = \frac{1}{a}\left(1 + \frac{\delta}{a}\right).$$

$$(2) \qquad \sqrt{a + \delta} = \sqrt{a}\left(1 + \frac{\delta}{2a}\right).$$

$$(3) \qquad \sqrt{a - \delta} = \sqrt{a}\left(1 - \frac{\delta}{2a}\right).$$

(4) Prove equation (7) above by putting $b = a + \delta$, where δ is small, and using Ex. 2.

As an example of the practical utility of these approximation formulæ, consider the correction of the barometric height for temperature. If a is the *relative* coefficient of linear expansion of the mercury with reference to the brass scale, and h the (uncorrected) barometric height at temperature $t°$ C., the correction to be added is—aht, to reduce to the reading at 0° C.

a for a brass scale = 0·000163.

Now under ordinary conditions, h and t will differ but slightly from 760 mm. and 16° C. respectively ;

$$\therefore \ h = 760 + k,$$
$$t = 15 + \delta,$$

where k and δ are small quantities compared with 760 and 15 respectively. Thus by formula (1)

$$ht = 760 \times 15 + 15k + 760\delta.$$

Writing $(h - 760)$ for k, and $(t - 15)$ for δ,

$$ht = 11400 + 15(h - 760) + 760(t - 15)$$
$$\therefore \ a \ ht = 1·86 + ·0024(h - 760) + 0·124(t - 15°).$$

(See Schuster and Lees, "Intermediate Practical Physics," § 2 ; Watson, "Text-Book of Practical Physics," Ch. I ; Roth, "Exercises in Physical Chemistry," trans. by Cameron, Ch. I.)

Examples :—

(1) Find the approximate values of the following :—

$(1·000024)(1·000065)$; $(1·00018)(0·99982)$;

$\dfrac{1}{1·000025}$; $\dfrac{1·00018}{0·99986}$. [1·000089 ; 1 ; 0·999975 ; 1·00032.]

(2) The formula for the expansion of a bar by heat is
$$l_t = l_0(1 + at),$$
where l_0 = length at 0° C.   Show that if heated from $t°$ to $t'°$ the final length is approximately
$$l_{t^1} = l_t(1 + at' - at).$$
(3) Prove similarly for the volume of a *liquid* :—
$$v_{t^1} = v_t(1 + \beta t' - \beta t).$$

Would this be true for a gas ? [No ; see the section on Taylor's Theorem.]

TABLE OF EXPONENTIAL AND LOGARITHMIC FUNCTIONS

The following table will furnish values for

$$y = \log_e x \text{ if } x \text{ is regarded as given,}$$
$$x = e^y \text{ if } y \text{ is regarded as given.}$$

Values intermediate between tabulated values may be obtained by interpolation with the Rule of Proportional Parts.

Examples :—

(1) Find $\log_e 125 \cdot 6$.

$$\text{Here } x = 125 \cdot 6 = 1 \cdot 256 \times 10^2$$
$$\therefore \log_e x = \log_e(1 \cdot 256 \times 10^2) = \log_e 1 \cdot 256 + 2 \log_e 10.$$
$$\text{Now } \log_e 1 \cdot 25 = 0 \cdot 2231,$$
$$\log_e 1 \cdot 26 = 0 \cdot 2311,$$
$$\therefore \frac{0 \cdot 2311 - 0 \cdot 2231}{1 \cdot 26 - 1 \cdot 25} = \frac{\log_e 1 \cdot 256 - 0 \cdot 2231}{1 \cdot 256 - 1 \cdot 25}$$
$$\therefore \log_e 1 \cdot 256 = 0 \cdot 2279$$
$$\therefore \log_e 125 \cdot 6 = 0 \cdot 2279 + 2 \times 2 \cdot 3026$$
$$= 4 \cdot 8331.$$

(2) Find the value of $e^{-2 \cdot 36}$.

Here $y = -2 \cdot 36$, or if we put $e^{-2 \cdot 36} = 1/e^{2 \cdot 36}$ we can evaluate $e^{-2 \cdot 36}$ if we find the value of $e^{2 \cdot 36}$. From the tables :—

$$\log_e 10 \cdot 50 = 2 \cdot 3513 \,; \; \log_e 10 \cdot 75 = 2 \cdot 3749.$$
$$\text{Hence if } x = e^{2 \cdot 36} :\!—$$
$$\frac{10 \cdot 75 - 10 \cdot 50}{2 \cdot 3749 - 2 \cdot 3513} = \frac{x - 10 \cdot 50}{2 \cdot 36 - 2 \cdot 3513}$$
$$\therefore x = 10 \cdot 558$$
$$\therefore e^{-2 \cdot 36} = 1 \div 10 \cdot 558 = 0 \cdot 09471.$$

x	y	x	y	x	y	x	y
1·00	0	1·51	·4121	2·02	·7031	2·53	·9282
1·01	·0099	1·52	·4187	2·03	·7080	2·54	·9322
1·02	·0198	1·53	·4253	2·04	·7129	2·55	·9361
1·03	·0296	1·54	·4318	2·05	·7178	2·56	·9400
1·04	·0392	1·55	·4383	2·06	·7227	2·57	·9439
1·05	·0488	1·56	·4447	2·07	·7275	2·58	·9478
1·06	·0583	1·57	·4511	2·08	·7324	2·59	·9517
1·07	·0677	1·58	·4574	2·09	·7372	2·60	·9555
1·08	·0770	1·59	·4637	2·10	·7419	2·61	·9594
1·09	·0862	1·60	·4700	2·11	·7467	2·62	·9632
1·10	·0953	1·61	·4762	2·12	·7514	2·63	·9670
1·11	·1044	1·62	·4824	2·13	·7561	2·64	·9708
1·12	·1133	1·63	·4886	2·14	·7608	2·65	·9746
1·13	·1222	1·64	·4947	2·15	·7655	2·66	·9783
1·14	·1310	1·65	·5008	2·16	·7701	2·67	·9821
1·15	·1398	1·66	·5068	2·17	·7747	2·68	·9858
1·16	·1484	1·67	·5128	2·18	·7793	2·69	·9895
1·17	·1570	1·68	·5188	2·19	·7839	2·70	·9933
1·18	·1655	1·69	·5247	2·20	·7885	2·71	·9969
1·19	·1740	1·70	·5306	2·21	·7930	2·72	1·0006
1·20	·1823	1·71	·5365	2·22	·7975	2·73	1·0043
1·21	·1906	1·72	·5423	2·23	·8020	2·74	1·0080
1·22	·1988	1·73	·5481	2·24	·8065	2·75	1·0116
1·23	·2070	1·74	·5539	2·25	·8109	2·76	1·0152
1·24	·2151	1·75	·5596	2·26	·8154	2·77	1·0188
1·25	·2231	1·76	·5653	2·27	·8198	2·78	1·0225
1·26	·2311	1·77	·5710	2·28	·8242	2·79	1·0260
1·27	·2390	1·78	·5766	2·29	·8286	2·80	1·0296
1·28	·2469	1·79	·5822	2·30	·8329	2·81	1·0332
1·29	·2546	1·80	·5878	2·31	·8372	2·82	1·0367
1·30	·2624	1·81	·5933	2·32	·8416	2·83	1·0403
1·31	·2700	1·82	·5988	2·33	·8458	2·84	1·0438
1·32	·2776	1·83	·6043	2·34	·8502	2·85	1·0473
1·33	·2852	1·84	·6098	2·35	·8544	2·86	1·0508
1·34	·2927	1·85	·6152	2·36	·8587	2·87	1·0543
1·35	·3001	1·86	·6206	2·37	·8629	2·88	1·0578
1·36	·3075	1·87	·6259	2·38	·8671	2·89	1·0613
1·37	·3148	1·88	·6313	2·39	·8713	2·90	1·0647
1·38	·3221	1·89	·6366	2·40	·8755	2·91	1·0682
1·39	·3293	1·90	·6419	2·41	·8796	2·92	1·0716
1·40	·3365	1·91	·6471	2·42	·8838	2·93	1·0750
1·41	·3436	1·92	·6523	2·43	·8879	2·94	1·0784
1·42	·3507	1·93	·6575	2·44	·8920	2·95	1·0813
1·43	·3577	1·94	·6627	2·45	·8961	2·96	1·0852
1·44	·3646	1·95	·6678	2·46	·9002	2·97	1·0886
1·45	·3716	1·96	·6729	2·47	·9042	2·98	1·0919
1·46	·3784	1·97	·6780	2·48	·9083	2·99	1·0953
1·47	·3853	1·98	·6831	2·49	·9123	3·00	1·0986
1·48	·3920	1·99	·6881	2·50	·9163	3·01	1·1019
1·49	·3988	2·00	·6931	2·51	·9203	3·02	1·1053
1·50	·4055	2·01	·6981	2·52	·9243	3·03	1·1086

x	y	x	y	x	y	x	y
3·04	1·1119	3·55	1·2669	4·06	1·4012	4·57	1·5195
3·05	1·1151	3·56	1·2698	4·07	1·4036	4·58	1·5217
3·06	1·1184	3·57	1·2726	4·08	1·4061	4·59	1·5239
3·07	1·1217	3·58	1·2754	4·09	1·4085	4·60	1·5261
3·08	1·1249	3·59	1·2782	4·10	1·4110	4·61	1·5282
3·09	1·1282	3·60	1·2809	4·11	1·4134	4·62	1·5304
3·10	1·1314	3·61	1·2837	4·12	1·4159	4·63	1·5326
3·11	1·1346	3·62	1·2865	4·13	1·4183	4·64	1·5347
3·12	1·1378	3·63	1·2892	4·14	1·4207	4·65	1·5369
3·13	1·1410	3·64	1·2920	4·15	1·4231	4·66	1·5390
3·14	1·1442	3·65	1·2947	4·16	1·4255	4·67	1·5412
3·15	1·1474	3·66	1·2975	4·17	1·4279	4·68	1·5433
3·16	1·1506	3·67	1·3002	4·18	1·4303	4.69	1·5454
3·17	1·1537	3·68	1·3029	4·19	1·4327	4·70	1·5476
3·18	1·1569	3·69	1·3056	4·20	1·4351	4·71	1·5497
3·19	1·1600	3·70	1·3083	4·21	1·4375	4·72	1·5518
3·20	1·1632	3·71	1·3110	4·22	1·4398	4·73	1·5539
3·21	1·1663	3·72	1·3137	4·23	1·4422	4·74	1·5560
3·22	1·1694	3·73	1·3164	4·24	1·4446	4·75	1·5581
3·23	1·1725	3·74	1·3191	4·25	1·4469	4·76	1·5602
3·24	1·1756	3·75	1·3218	4·26	1·4493	4·77	1·5623
3·25	1·1787	3·76	1·3244	4·27	1·4516	4·78	1·5644
3·26	1·1817	3·77	1·3271	4·28	1·4540	4·79	1·5665
3·27	1·1848	3·78	1·3297	4·29	1·4563	4·80	1·5686
3·28	1·1878	3·79	1·3324	4·30	1·4586	4·81	1·5707
3·29	1·1909	3·80	1·3350	4·31	1·4609	4·82	1·5728
3·30	1·1939	3·81	1·3376	4·32	1·4633	4·83	1·5748
3·31	1·1969	3·82	1·3403	4·33	1·4656	4·84	1·5769
3·32	1·1999	3·83	1·3429	4·34	1·4679	4·85	1·5790
3·33	1·2030	3·84	1·3455	4·35	1·4702	4·86	1·5810
3·34	1·2060	3·85	1·3481	4·36	1·4725	4·87	1·5831
3·35	1·2090	3·86	1·3507	4·37	1·4748	4·88	1·5851
3·36	1·2119	3·87	1·3533	4·38	1·4770	4·89	1·5872
3·37	1·2149	3·88	1·3558	4·39	1·4793	4·90	1·5892
3·38	1·2179	3·89	1·3584	4·40	1·4816	4·91	1·5913
3·39	1·2208	3·90	1·3610	4·41	1·4839	4·92	1·5933
3·40	1·2238	3·91	1·3635	4·42	1·4861	4·93	1·5953
3·41	1·2267	3·92	1·3661	4·43	1·4884	4·94	1·5974
3·42	1·2296	3·93	1·3686	4·44	1·4907	4·95	1·5994
3·43	1·2326	3·94	1·3712	4·45	1·4929	4·96	1·6014
3·44	1·2355	3·95	1·3737	4·46	1·4951	4·97	1·6034
3·45	1·2384	3·96	1·3762	4·47	1·4974	4·98	1·6054
3·46	1·2413	3·97	1·3788	4·48	1·4996	4·99	1·6074
3·47	1·2442	3·98	1·3813	4·49	1·5019	5·00	1·6094
3·48	1·2470	3·99	1·3838	4·50	1·5041	5·01	1·6114
3·49	1·2499	4·00	1·3863	4·51	1·5063	5·02	1·6134
3·50	1·2528	4·01	1·3888	4·52	1·5085	5·03	1·6154
3·51	1·2556	4·02	1·3913	4·53	1·5107	5·04	1·6174
3·52	1·2585	4·03	1·3938	4·54	1·5129	5·05	1·6194
3·53	1·2613	4·04	1·3962	4·55	1·5151	5·06	1·6214
3·54	1·2641	4·05	1·3987	4·56	1·5173	5·07	1·6233

x	y	x	y	x	y	x	y
5·08	1·6253	5·59	1·7210	6·10	1·8083	6·61	1·8886
5·09	1·6273	5·60	1·7228	6·11	1·8099	6·62	1·8901
5·10	1·6292	5·61	1·7246	6·12	1·8116	6·63	1·8916
5·11	1·6312	5·62	1·7263	6·13	1·8132	6·64	1·8931
5·12	1·6332	5·63	1·7281	6·14	1·8148	6·65	1·8946
5·13	1·6351	5·64	1·7299	6·15	1·8165	6·66	1·8961
5·14	1·6371	5·65	1·7317	6·16	1·8181	6·67	1·8976
5·15	1·6390	5·66	1·7334	6·17	1·8197	6·68	1·8991
5·16	1·6409	5·67	1·7352	6·18	1·8213	6·69	1·9006
5·17	1·6429	5·68	1·7370	6·19	1·8229	6·70	1·9021
5·18	1·6448	5·69	1·7387	6·20	1·8245	6·71	1·9036
5·19	1·6467	5·70	1·7405	6·21	1·8262	6·72	1·9051
5·20	1·6487	5·71	1·7422	6·22	1·8278	6·73	1·9066
5·21	1·6506	5·72	1·7440	6·23	1·8294	6·74	1·9081
5·22	1·6525	5·73	1·7457	6·24	1·8310	6·75	1·9095
5·23	1·6544	5·74	1·7475	6·25	1·8326	6·76	1·9110
5·24	1·6563	5·75	1·7492	6·26	1·8342	6·77	1·9125
5·25	1·6582	5·76	1·7509	6·27	1·8358	6·78	1·9140
5·26	1·6601	5·77	1·7527	6·28	1·8374	6·79	1·9155
5·27	1·6620	5·78	1·7544	6·29	1·8390	6·80	1·9169
5·28	1·6639	5·79	1·7561	6·30	1·8405	6·81	1·9184
5·29	1·6658	5·80	1·7579	6·31	1·8421	6·82	1·9199
5·30	1·6677	5·81	1·7596	6·32	1·8437	6·83	1·9213
5·31	1·6696	5·82	1·7613	6·33	1·8453	6·84	1·9228
5·32	1·6715	5·83	1·7630	6·34	1·8469	6·85	1·9242
5·33	1·6734	5·84	1·7647	6·35	1·8485	6·86	1·9257
5·34	1·6752	5·85	1·7664	6·36	1·8500	6·87	1·9272
5·35	1·6771	5·86	1·7681	6·37	1·8516	6·88	1·9286
5·36	1·6790	5·87	1·7699	6·38	1·8532	6·89	1·9301
5·37	1·6808	5·88	1·7716	6·39	1·8547	6·90	1·9315
5·38	1·6827	5·89	1·7733	6·40	1·8563	6·91	1·9330
5·39	1·6845	5·90	1·7750	6·41	1·8579	6·92	1·9344
5·40	1·6864	5·91	1·7766	6·42	1·8594	6·93	1·9359
5·41	1·6882	5·92	1·7783	6·43	1·8610	6·94	1·9373
5·42	1·6901	5·93	1·7800	6·44	1·8625	6·95	1·9387
5·43	1·6919	5·94	1·7817	6·45	1·8641	6·96	1·9402
5·44	1·6938	5·95	1·7834	6·46	1·8656	6·97	1·9416
5·45	1·6956	5·96	1·7851	6·47	1·8672	6·98	1·9430
5·46	1·6974	5·97	1·7867	6·48	1·8687	6·99	1·9445
5·47	1·6993	5·98	1·7884	6·49	1·8703	7·00	1·9459
5·48	1·7011	5·99	1·7901	6·50	1·8718	7·01	1·9473
5·49	1·7029	6·00	1·7918	6·51	1·8733	7·02	1·9488
5·50	1·7047	6·01	1·7934	6·52	1·8749	7·03	1·9502
5·51	1·7066	6·02	1·7951	6·53	1·8764	7·04	1·9516
5·52	1·7084	6·03	1·7967	6·54	1·8779	7·05	1·9530
5·53	1·7102	6·04	1·7984	6·55	1·8795	7·06	1·9544
5·54	1·7120	6·05	1·8001	6·56	1·8810	7·07	1·9559
5·55	1·7138	6·06	1·8017	6·57	1·8825	7·08	1·9573
5·56	1·7156	6·07	1·8034	6·58	1·8840	7·09	1·9587
5·57	1·7174	6·08	1·8050	6·59	1·8856	7·10	1·9601
5·58	1·7192	6·09	1·8066	6·60	1·8871	7·11	1·9615

x	y	x	y	x	y	x	y
7·12	1·9629	7·63	2·0321	8·14	2·0968	8·65	2·1576
7·13	1·9643	7·64	2·0334	8·15	2·0980	8·66	2·1587
7·14	1·9657	7·65	2·0347	8·16	2·0992	8·67	2·1599
7·15	1·9671	7·66	2·0360	8·17	2·1005	8·68	2·1610
7·16	1·9685	7·67	2·0373	8·18	2·1017	8·69	2·1622
7·17	1·9699	7·68	2·0386	8·19	2·1029	8·70	2·1633
7·18	1·9713	7·69	2·0399	8·20	2·1041	8·71	2·1645
7·19	1·9727	7·70	2·0412	8·21	2·1054	8·72	2·1656
7·20	1·9741	7·71	2·0425	8·22	2·1066	8·73	2·1668
7·21	1·9755	7·72	2·0438	8·23	2·1078	8·74	2·1679
7·22	1·9769	7·73	2·0451	8·24	2·1090	8·75	2·1691
7·23	1·9782	7·74	2·0464	8·25	2·1102	8·76	2·1702
7·24	1·9796	7·75	2·0477	8·26	2·1114	8·77	2·1713
7·25	1·9810	7·76	2·0490	8·27	2·1126	8·78	2·1725
7·26	1·9824	7·77	2·0503	8·28	2·1138	8·79	2·1736
7·27	1·9838	7·78	2·0516	8·29	2·1150	8·80	2·1748
7·28	1·9851	7·79	2·0528	8·30	2·1162	8·81	2·1759
7·29	1·9865	7·80	2·0541	8·31	2·1175	8·82	2·1770
7·30	1·9879	7·81	2·0554	8·32	2·1187	8·83	2·1782
7·31	1·9892	7·82	2·0567	8·33	2·1199	8·84	2·1793
7·32	1·9906	7·83	2·0580	8·34	2·1211	8·85	2·1804
7·33	1·9920	7·84	2·0592	8·35	2·1223	8·86	2·1815
7·34	1·9933	7·85	2·0605	8·36	2·1235	8·87	2·1827
7·35	1·9947	7·86	2·0618	8·37	2·1247	8·88	2·1838
7·36	1·9961	7·87	2·0631	8·38	2·1258	8·89	2·1849
7·37	1·9974	7·88	2·0643	8·39	2·1270	8·90	2·1861
7·38	1·9988	7·89	2·0656	8·40	2·1282	8·91	2·1872
7·39	2·0001	7·90	2·0669	8·41	2·1294	8·92	2·1883
7·40	2·0015	7·91	2·0681	8·42	2·1306	8·93	2·1894
7·41	2·0028	7·92	2·0694	8·43	2·1318	8·94	2·1905
7·42	2·0042	7·93	2·0707	8·44	2·1330	8·95	2·1917
7·43	2·0045	7·94	2·0719	8·45	2·1342	8·96	2·1928
7·44	2·0069	7·95	2·0732	8·46	2·1353	8·97	2·1939
7·45	2·0082	7·96	2·0744	8·47	2·1365	8·98	2·1950
7·46	2·0096	7·97	2·0757	8·48	2·1377	8·99	2·1961
7·47	2·0109	7·98	2·0769	8·49	2·1389	9·00	2·1972
7·48	2·0122	7·99	2·0782	8·50	2·1401	9·01	2·1983
7·49	2·0136	8·00	2·0794	8·51	2·1412	9·02	2·1994
7·50	2·0149	8·01	2·0807	8·52	2·1424	9·03	2·2006
7·51	2·0162	8·02	2·0819	8·53	2·1436	9·04	2·2017
7·52	2·0176	8·03	2·0832	8·54	2·1448	9·05	2·2028
7·53	2·0189	8·04	2·0844	8·55	2·1459	9·06	2·2039
7·54	2·0202	8·05	2·0857	8·56	2·1471	9·07	2·2050
7·55	2·0215	8·06	2·0869	8·57	2·1483	9·08	2·2061
7·56	2·0229	8·07	2·0882	8·58	2·1492	9·09	2·2072
7·57	2·0242	8·08	2·0894	8·59	2·1506	9·10	2·2083
7·58	2·0255	8·09	2·0906	8·60	2·1518	9·11	2·2094
7·59	2·0268	8·10	2·0919	8·61	2·1529	9·12	2·2105
7·60	2·0281	8·11	2·0931	8·62	2·1541	9·13	2·2116
7·61	2·0295	8·12	2·0943	8·63	2·1552	9·14	2·2127
7·62	2·0308	8·13	2·0956	8·64	2·1564	9·15	2·2138

x	y	x	y	x	y	x	y
9·16	2·2148	9·53	2·2544	9·89	2·2915	17·50	2·8621
9·17	2·2159	9·54	2·2555	9·90	2·2925	18·00	2·8904
9·18	2·2170	9·55	2·2565	9·91	2·2935	18·50	2·9173
9·19	2·2181	9·56	2·2576	9·92	2·2946	19·00	2·9444
9·20	2·2192	9·57	2·2586	9·93	2·2956	19·50	2·9703
9·21	2·2203	9·58	2·2597	9·94	2·2966	20·00	2·9957
9·22	2·2214	9·59	2·2607	9·95	2·2976	21·00	3·0445
9·23	2·2225	9·60	2·2618	9·96	2·2986	22·00	3·0911
9·24	2·2235	9·61	2·2628	9·97	2·2996	23·00	3·1355
9·25	2·2246	9·62	2·2638	9·98	2·3006	24·00	3·1781
9·26	2·2257	9·63	2·2649	9·99	2·3016	25·00	3·2189
9·27	2·2268	9·64	2·2659	10·00	2·3026	26·00	3·2581
9·28	2·2279	9·65	2·2670	10·25	2·3279	27·00	3·2958
9·29	2·2289	9·66	2·2680	10·50	2·3513	28·00	3·3322
9·30	2·2300	9·67	2·2690	10·75	2·3749	29·00	3·3673
9·31	2·2311	9·68	2·2701	11·00	2·3979	30·00	3·4012
9·32	2·2322	9·69	2·2711	11·25	2·4201	31·00	3·4340
9·33	2·2332	9·70	2·2721	11·50	2·4430	32·00	3·4657
9·34	2·2343	9·71	2·2732	11·75	2·4636	33·00	3·4965
9·35	2·2354	9·72	2·2742	12·00	2·4849	34·00	3·5263
9·36	2·2364	9·73	2·2752	12·25	2·5052	35·00	3·5553
9·37	2·2375	9·74	2·2762	12·50	2·5262	36·00	3·5835
9·38	2·2386	9·75	2·2773	12·75	2·5455	37·00	3·6101
9·39	2·2396	9·76	2·2783	13·00	2·5649	38·00	3·6376
9·40	2·2407	9·77	2·2793	13·25	2·5840	39·00	3·6636
9·41	2·2418	9·78	2·2803	13·50	2·6027	40·00	3·6889
9·42	2·2428	9·79	2·2814	13·75	2·6211	41·00	3·7136
9·43	2·2439	9·80	2·2824	14·00	2·6391	42·00	3·7377
9·44	2·2450	9·81	2·2834	14·25	2·6567	43·00	3·7612
9·45	2·2460	9·82	2·2844	14·50	2·6740	44·00	3·7842
9.46	2·2471	9·83	2·2854	14·75	2·6913	45·00	3·8067
9·47	2·2481	9·84	2·2865	15·00	2·7081	46·00	3·8286
9·48	2·2492	9·85	2·2875	15·50	2·7408	47·00	3·8501
9·49	2·2502	9·86	2·2885	16·00	2·7726	48·00	3·8712
9·50	2·2513	9·87	2·2895	16·50	2·8034	49·00	3·8918
9·51	2·2523	9·88	2·2905	17·00	2·8332	50·00	3·9120
9·52	2·2534						

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anthropomorphic
mnemonic